AQUATIC CRITICAL LOADS AND EXCEEDANCES IN ACID-SENSITIVE PORTIONS OF VIRGINIA AND WEST VIRGINIA

Results of Southeastern Multiagency Critical Loads Research Project

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TABLE OF CONTENTS

List of Figures

List of Tables

Executive Summary

Background

The critical load (CL) is the level of sustained atmospheric deposition of S, N, or acidity below which significant harm to sensitive ecosystems does not occur according to current scientific understanding. For the sensitive receptor stream water, the most commonly selected chemical indicator is acid neutralizing capacity (ANC). A number of critical criteria values of ANC have been used as the basis for CL calculations, the most common of which have been 0, 20, 50, and 100 μeq/L. Each is believed to be associated with biological responses. The steady state CL can be calculated using an empirical model. Results are reported here for a pilot project to explore approaches to CL calculation and mapping for the southeastern United States.

The most commonly used steady state CL model for aquatic resource protection is the Steady State Water Chemistry (SSWC) model (Henriksen and Posch 2001). In this approach, the CL is calculated as a simple balancing of watershed base cation (BC; e.g., Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) inputs and outputs with the atmospheric deposition of strong acids.

The watershed supply of BC due to weathering (BC_w) is the CL model parameter that generally has the most influence in the CL calculation. Regional approaches for estimating BC_w are uncertain, in that they are rooted in unsubstantiated assumptions and rely on data that may not be available at appropriate scales for sensitive watersheds. Because the CL is a theoretical construct, its estimation by any model cannot be directly confirmed or validated, at least in the short term.

Estimation of Base Cation Weathering

An important objective of the research reported here is to explore an alternative approach for estimating BC_w, arguably the key term for estimating CL using the SSWC model (or any other aquatic steady state CL model). The dynamic model MAGIC (Model of Acidification of Groundwater in Catchments; Cosby et al. 1985) was used to estimate watershed-specific values of effective BC_w. Based on empirical relationships between simulated BC_w and key stream chemistry variables and watershed characteristics, simulated BC_w and other spatial variables were extrapolated to the regional population of stream watersheds in acid-sensitive portions of Virginia and West Virginia, allowing regional calculation of CL and CL exceedance using SSWC.

Regression techniques were used to establish equations for BC_w prediction across the landscape within each of three study ecoregions (Blue Ridge, Ridge and Valley, and Central Appalachian). MAGIC model estimates of BC_w for the calibrated watersheds located throughout the study area were used as modeled weathering rates. Two predictor equations were established for each of the three ecoregions, one using both landscape characteristics and water chemistry parameters for use in the 522 watersheds for which stream chemistry data were available (estimated BC_w with water chemistry) and another using landscape characteristics only (estimated BC_w without water chemistry). Continuous upslope averages for each of the landscape predictor variables were calculated for each 30-m grid cell using hydrologically conditioned digital elevation model (DEM) data derivatives. This approach was used because stream chemistry integrates conditions throughout the drainage area.

A total of 92 stream sites were successfully calibrated using MAGIC. BC_w estimates for those watersheds were extracted from the model calibration files and used as inputs for SSWC calculations.

Calculation of Critical Load

The stream network generated from the DEM for the pilot project study region was based on a minimum contributing area of 0.5 km^2. In other words, the minimum drainage area that was designated as a stream watershed from the flow accumulation analysis was 0.5 km^2. The lower boundary of each watershed was determined on the basis of stream tributary junctions. This process resulted in generation of a topographically determined stream network that was intermediate in stream size and density between the 1:100,000 National Hydrography Dataset (NHD) moderate resolution stream network and the high resolution 1:24,000 NHD network. The typical topographically determined watersheds were on the order of 1 km^2 in area.

Values for each of the terms in the SSWC model were calculated for every 30-m grid cell in the study region. The SSWC equation was then solved to yield an estimate of CL for each 30-m grid cell. The representative watershed CL value was then calculated for each topographically determined watershed as an average of the CL values calculated at each stream cell (each grid cell intercepted by a topographically determined stream) within the watershed. A regional watershed CL map was prepared for each critical ANC indicator value.

Critical load results were also depicted for the network of streams that flow through these watersheds. Results of the CL calculations for the stream pixels (each 30-m grid cell that

intersected a topographically determined stream) were averaged to reflect the CL of the stream reach that flows through that watershed based on the national stream network as represented in the high-resolution NHD database. This process was completed for all watersheds to yield a regional stream coverage that is coded with CL according to the value given to its associated watershed.

For the study area as a whole, about 30 to 40% of the stream length (depending on selection of threshold ANC value) was classified as having CL above 200 meq/m^2/yr. The remainder of the stream length had lower calculated CL values, with about one-fourth of the stream length having CL below 100 meq/m^2/yr. For most CL classes, there was not much difference in the extent of stream length within the class as influenced by the threshold ANC value selected. For the lowest CL class (less than 50 meq/m^2/yr), however, choice of threshold ANC value made a substantial difference to the stream length calculations. The length of stream estimated to have CL $\leq$ 50 meq/m^2/yr across the study area varied by about a factor of four depending on which threshold ANC value was selected.

Critical loads were generally much lower and more heavily influenced by selection of the threshold ANC value for Wilderness streams as compared with non-Wilderness streams. About 70% of the Wilderness stream length had CL less than 100 meq/m^2/yr to protect to stream ANC above 50 μeq/L. Nearly half of the Wilderness stream length had CL less than 100 meq/m^2/yr to protect to stream ANC above zero.

Critical Load Exceedance

Watershed averaged values of total ambient deposition of acidity were overlayed with the CL maps to generate regional estimates of CL exceedance, to identify areas where ambient deposition exceeds the CL. Broad areas of the study region were found to be in CL exceedance when compared to the 5-year average deposition centered on 2005. Such areas are disproportionately associated with Class I areas and other public lands.

Half of the stream length within the study region was calculated to receive current acidic deposition in exceedance of the CL to protect against stream ANC below zero. That percentage increased to 53% for the threshold ANC value of 20 μeq/L, to 57% for the threshold ANC value of 50 μeq/L, and 63% for the threshold ANC value of 100 μeq/L. Nearly one-fourth of the stream length in the study region was estimated to be receiving acidic deposition that is more than double the CL for protecting stream ANC from going below 50 μeq/L. Exceedance of the

CL was most prevalent in the Blue Ridge ecoregion, followed by the Central Appalachian ecoregion.

Temporal Patterns of Response

The CL and CL exceedance values calculated in this project pertain to long-term, steady-state water quality conditions. It may take a long time to reach the steady-state condition with respect to deposition acidity and stream chemistry at a constant loading rate. To address this concern, the dynamic model MAGIC was used to estimate the time to reach steady state at the CL deposition values calculated using the SSWC model. Results showed that:

- most of the modeled watersheds will not reach steady state for hundreds of years, and
- the time period is somewhat longer if the selected threshold ANC value is higher (more protective).

Summary

In summary, the SSWC steady state CL model was applied in a regional pilot study to estimate CLs and exceedances for aquatic resources in streams in the southeastern U.S. Terms in the SSWC model were derived on a regional landscape basis. Estimates of BC deposition and BC uptake by forests were available from national network databases. A computationally efficient and robust method for estimating weathering on a continuous basis across a regional landscape was developed for this project. It was based on weathering estimates extracted from a well-tested process-based watershed model of drainage water acid-base chemistry and also on features of the landscape that are available as regional spatial data coverages. This approach avoids many of the uncertainties associated with other common methods for estimating BC_w for input into SSWC and other steady state CL models.

Results indicate that more than half of the streams within the study region receive current acidic deposition that is higher than the steady state CLs. Furthermore, results indicate that most of the modeled watersheds will likely not reach the steady state condition for hundreds of years after continuous constant deposition at the CL levels are established.

It should be noted that CL and exceedance calculations and maps reported here represent examples of one approach to the CL process. No formal uncertainly analysis has been conducted. Therefore, the confidence level associated with these results is not known. Further research is needed to test, evaluate, and refine the approaches used to quantify weathering and CL.

1.0 INTRODUCTION

Atmospheric deposition of sulfur (S) and nitrogen (N), derived from utility, industrial, and nonpoint air pollution sources, has caused acidification of soils, soil water, and drainage water across broad areas of the eastern United States (Greaver et al. 2008). Such acidification has been associated with enhanced leaching of sulfate (SO_4^{2-}) and nitrate (NO_3^-) to drainage waters, depletion of calcium (Ca^{2+}) and other nutrient cations from soil, reduced pH and acid neutralizing capacity (ANC) of surface waters, and increased mobilization of potentially toxic inorganic aluminum (Al_i; Sullivan 2000). Resulting biological effects have included toxicity to fish and aquatic invertebrates and adverse impacts on forest vegetation, especially red spruce and sugar maple trees (U.S. EPA 2009). Aquatic effects have been better documented and appear to be more widespread than terrestrial effects, and have been especially pronounced in Monongahela National Forest in West Virginia (Sullivan and Cosby 2004), Shenandoah National Park in Virginia (Sullivan et al. 2003), and other forested mountainous areas of western Virginia (Cosby et al. 2001).

Resource managers are now confronted with the need for air pollution emissions reductions sufficient to allow damaged resources to recover. In order to inform public policy regarding air pollutant emissions controls, it is important to determine 1) the level of emissions, and associated atmospheric deposition, that are associated with varying degrees of chemical effects and 2) the associations between water and soil chemistry and consequent biological impacts. One of the most important tools available to natural resource managers in this context involves model calculation of critical loads (CLs).

The CL is the level of sustained atmospheric deposition of S, N, or acidity below which significant harm to sensitive ecosystems does not occur according to current scientific understanding (Nilsson and Grennfelt 1988). The CL process typically involves selection of one or more sensitive receptor(s), one or more chemical indicator(s) of biological response for the sensitive receptor(s) of concern, and one or more critical chemical indicator criteria (or threshold) values that have been shown to be associated with adverse biological impacts. For the sensitive receptor stream water, the most commonly selected chemical indicator is ANC. A number of critical criteria values of ANC have been used as the basis for CL calculations, the most common of which have been 0, 20, 50, and 100 μeq/L. The first two levels approximately correspond in the Appalachian Mountains region to chronic and episodic effects on brook trout,

respectively (Bulger et al. 1999). An ANC threshold of 50 to 100 μeq/L is believed to be protective of general ecological health (cf., Cosby et al. 2006, U.S. EPA 2009).

The CL is generally calculated as a long-term steady state condition (Nilsson and Grennfelt 1988). It represents the amount of acidic deposition that is expected to result in achieving a particular stream ANC (or other designated receptor threshold value) over the long term. Under constant atmospheric deposition at the determined CL, however, it may take many decades or centuries for the sensitive chemical indicator (i.e., stream ANC) to reach the designated threshold ANC value.

The steady state CL for protection of either aquatic or terrestrial resources can be calculated using a simple mass balance, of which there are several alternative approaches. The most commonly used steady state CL modeling approach for aquatic resource protection is the Steady State Water Chemistry (SSWC) model (Henriksen and Posch 2001), which is calculated as a simple balancing of watershed base cation (BC; e.g., Ca^{2+}, Mg^{2+}, K^+) inputs and outputs.

$$CL(A) = BC_{dep} + BC_{w} - Bc_{up} - ANC_{limit} \tag{1}$$

The inputs to the subject watershed are base cation weathering (BC_w) and atmospheric deposition (BC_{dep}). The outputs include base cation nutrient (i.e., Ca^{2+}, Mg^{2+}, K^+) uptake by tree boles that are removed from the watershed through timber harvest (Bc_{up}). Vegetative uptake into plant material that is not harvested does not represent an output term in the model, as the BCs in non-harvested woody materials are largely recycled within the watershed rather than being transported out of the watershed.

Also included in the model with the BC output terms is a buffer, or allowance, for the BCs needed to support ecosystem health. In the SSWC and other aquatic CL approaches, this buffer is expressed as an ANC leaching flux (ANC_{limit}), which is calculated as the product of the selected threshold ANC value multiplied by water runoff. This BC buffer is needed to maintain surface water ANC at the designated level that is expected to support healthy fisheries and aquatic communities. The threshold ANC value is often set at 0, 20, 50, and/or 100 μeq/L. Data available within the pilot study area with which to evaluate aquatic biological response functions are summarized in Appendix A.

Critical load studies in North America have mainly been undertaken in Canada (cf., Henriksen and Dillon 2001, Ouimet et al. 2006), where the CLs have been used to design emissions reduction programs (Jeffries and Lam 1993, RMCC 1990). Much of this work was

presented, along with steady state CL maps for eastern Canada, in the 2004 Canadian Acid Deposition Science Assessment (Jeffries et al. 2005). Dupont et al. (2005) estimated CLs and exceedances for lakes in eastern Canada and New England. Most other aquatic CLs studies in the U.S. have focused on smaller sub-regional areas or individual watersheds (cf., Sullivan et al. 2003, Sullivan and Cosby 2004).

While the concepts expressed in the definition of CLs are conceptually easy to understand, CL application requires careful consideration of a number of terms and procedures. It is apparent that there can be many different CL values for a given atmospheric pollutant depending on the receptor or sensitive element(s) being considered. Furthermore, the same atmospheric pollutant can produce a variety of different disturbances in a sensitive ecosystem that might occur at different pollutant loads. For example, N deposition produces both nutrient (eutrophication) and acidification effects, and the CL of N for each type of disturbance may be different.

The watershed supply of BC due to weathering is the CL model parameter that typically has the most influence in the CL calculation and has the largest uncertainty (Li and McNulty 2007, U.S. EPA 2009, McDonnell et al. in review). In essence, the maintenance of long-term aquatic ecosystem acid-base chemistry health depends on keeping the atmospheric acid load relatively low compared with the natural re-supply of BCs through weathering, Thus, CL is controlled largely by BC_w. If the estimate of BC_w is based on a faulty approach or insufficient data, and is therefore inaccurate, the resulting CL calculation may be of little value for its intended purpose: supporting resource management decision-making.

The most common methods for estimating BC_w for inclusion in the SSWC model involve either use of regional estimates of soil substrate and clay content or simple empirical calculations designed to estimate what the level of historical weathering would have to have been in order to support the observed current concentrations of BC in drainage water (Henriksen and Posch 2001). The former approach assumes that weathering varies with soil clay content and geologic substrate in ways that can be represented by available spatial soils and geologic data. Inputs to the soil clay/substrate approach to estimation of BC_w include mean annual air temperature, soil depth, % clay, and geologic type. The geologic types are acidic (e.g., granites, gneiss, sandstones, felsic rocks), intermediate (e.g., diorite, granodiorite, conglomerate, and most sedimentary rocks other than sandstone), and basic (e.g., mafic rocks, carbonates; Pardo and Duarte 2007). It is assumed that the lowest weathering rates will occur with cold temperatures, in

shallow soils having low clay content, over acidic rock types (Sverdrup et al. 1990). The latter approach entails a number of assumptions about background pre-industrial water chemistry and the extent to which the base cation flux in drainage water has been changed in response to increased leaching of SO_4^{2-} and/or NO_3^- (the so-called F-factor approach; cf., Henriksen 1984, Henrikson and Posch 2001).

Both approaches discussed above are uncertain, in that they are rooted in unsubstantiated assumptions and rely on data that may not be available at appropriate scales for the sensitive watersheds within a given region of interest. Published studies based on the approach that assumes weathering varies with clay content and substrate use empirical regressions to quantify these relationships. The reported empirical regressions all use European soil and substrate data at high latitudes (cooler temperatures) and may not be expected to yield realistic values when applied outside of these conditions. There are no published accounts of empirical regression relationships developed for North America.

A primary objective of the research reported here is to explore an alternative approach for estimating BC_w, arguably the key term for estimating CL using the SSWC model (or any other aquatic steady state CL model). The dynamic model, MAGIC (Model of Acidification of Groundwater in Catchments; Cosby et al. 1985), was used to estimate watershed-specific values of effective BC_w for a suite of modeled streams. Based on empirical relationships between simulated BC_w and key stream chemistry variables and watershed characteristics, simulated BC_w and other spatial variables were extrapolated to the regional population of streams in acid-sensitive portions of Virginia and West Virginia, allowing regional calculation of CL and CL exceedance using SSWC. MAGIC is used here as a tool to estimate BC_w because 1) there are no rigorous estimates of BC_w for this region derived using other approaches, 2) MAGIC is a dynamic model that includes representation of major processes known to control acidification response, and 3) MAGIC has been well tested and confirmed in a number of studies (cf., Sullivan and Cosby 1995, Cosby et al. 1996, Sullivan et al. 1996).

Application of the SSWC model to the study region in Virginia and West Virginia allows estimation of potential risks and current extent of impact to streams across a large geographic area. This area shows spatial variation in both acidification sensitivity and air pollution exposure. It also shows spatial variability in land use, including substantial amounts of protected federal lands. Class I national park and designated Wilderness areas within the study region are afforded

the highest level of protection against adverse impacts of air pollution by the Clean Air Act (cf., Sullivan et al. 2003).

The work reported here is one part of a pair of linked projects, broadly termed the "multiagency critical loads effort for the eastern United States". This project focuses on estimation of steady state aquatic CL values for streams in Virginia and West Virginia. Ecosystem Research Group, Ltd. is conducting the companion project, which is estimating steady state terrestrial and aquatic (lake) CL values in New England and New York, as a follow-up to earlier efforts performed on behalf of the Joint Conference of New England Governors and Eastern Canadian Premiers (Dupont et al. 2005). In addition, the Northeast States for Coordinated Air Use Management (NESCAUM) stakeholder group is coordinating outreach for the multiagency effort through state air quality agencies.

2.0 APPROACH

The major steps involved in developing CL and exceedance maps for the study region were as follows:

1. Assemble spatial data layers for each term in the CL equation
   a.) create weathering overlay
   b) create runoff overlay
   c) generate regional estimates of wet and dry atmospheric deposition
   d) generate forest uptake overlay
2. Estimate N uptake parameter values
3. Calculate regional CL values for the landscape
4. Transfer regional CL values from the landscape to the stream network
5. Calculate CL exceedances

2.1 Site Selection and Data Sources

The study area was defined as the portions of the Central Appalachian, Ridge and Valley, and Blue Ridge Omernik Level III Ecoregions that occur within the states of Virginia and West Virginia (Figure 1). Available water chemistry data were compiled for 522 streams from previous studies in acid-sensitive portions of VA and WV (cf., Sullivan et al. 2002, 2003; Sullivan and Cosby 2004). There are substantial numbers of known acidic (ANC ≤ 0 μeq/L) and low-ANC streams throughout the study region (Figure 2). Many of these acid sensitive streams occur on public lands, including national park, wilderness, and national forest lands (Figure 3).

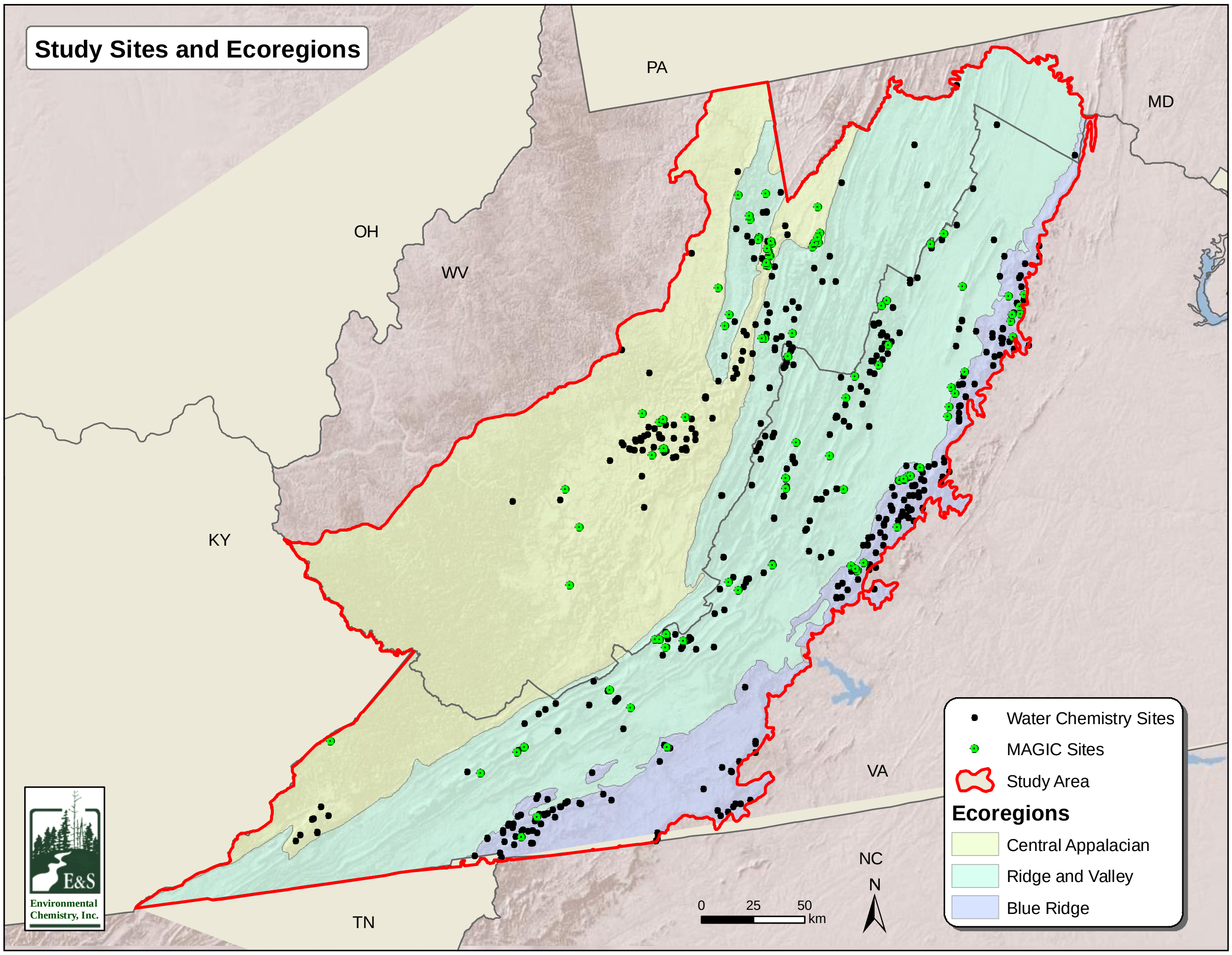


Figure 1. Study area selected for this research, showing the three ecoregions and locations of streams having water chemistry and those for which MAGIC model calibrations were available.

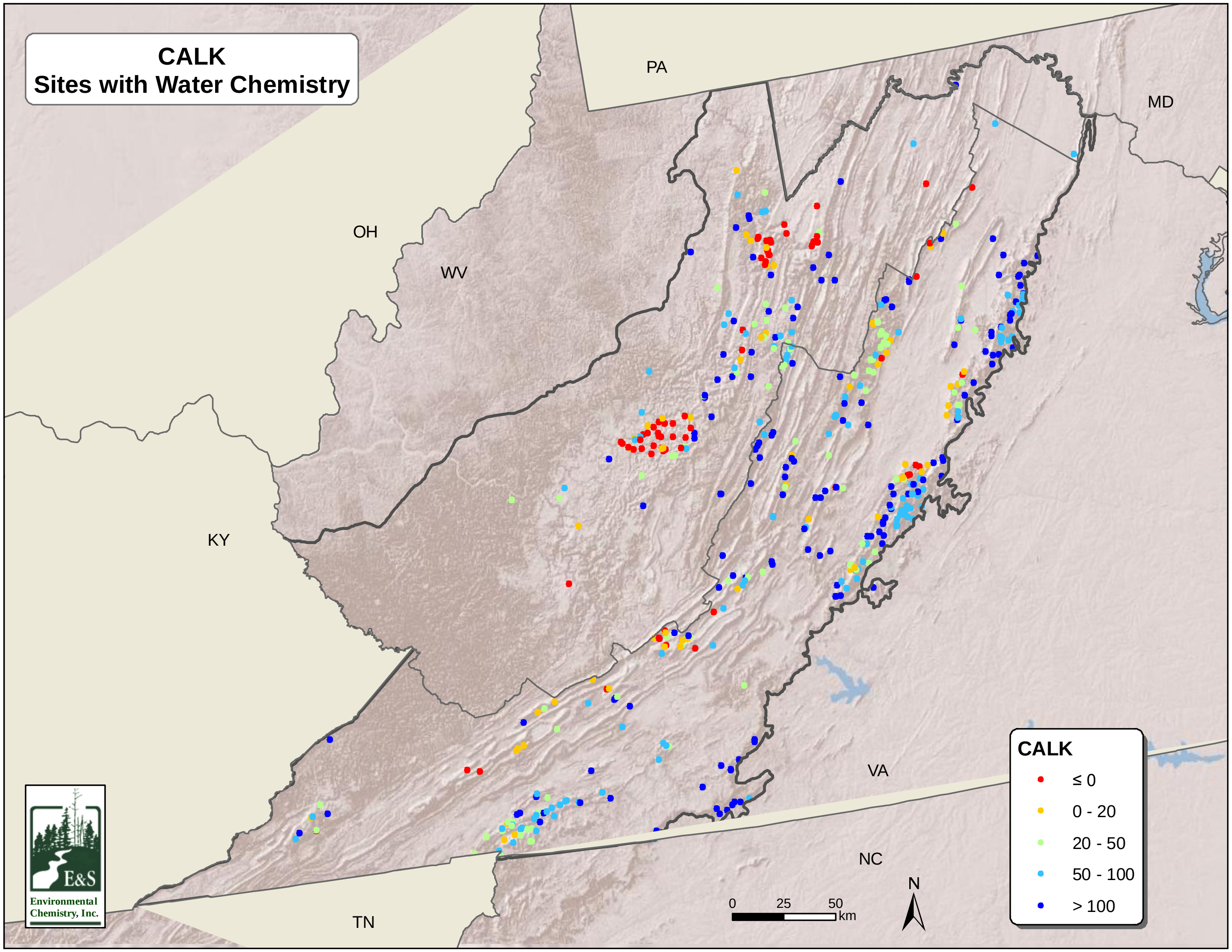


Figure 2. Calculated ANC (CALK) values of streams within the study region for which water chemistry data are available.

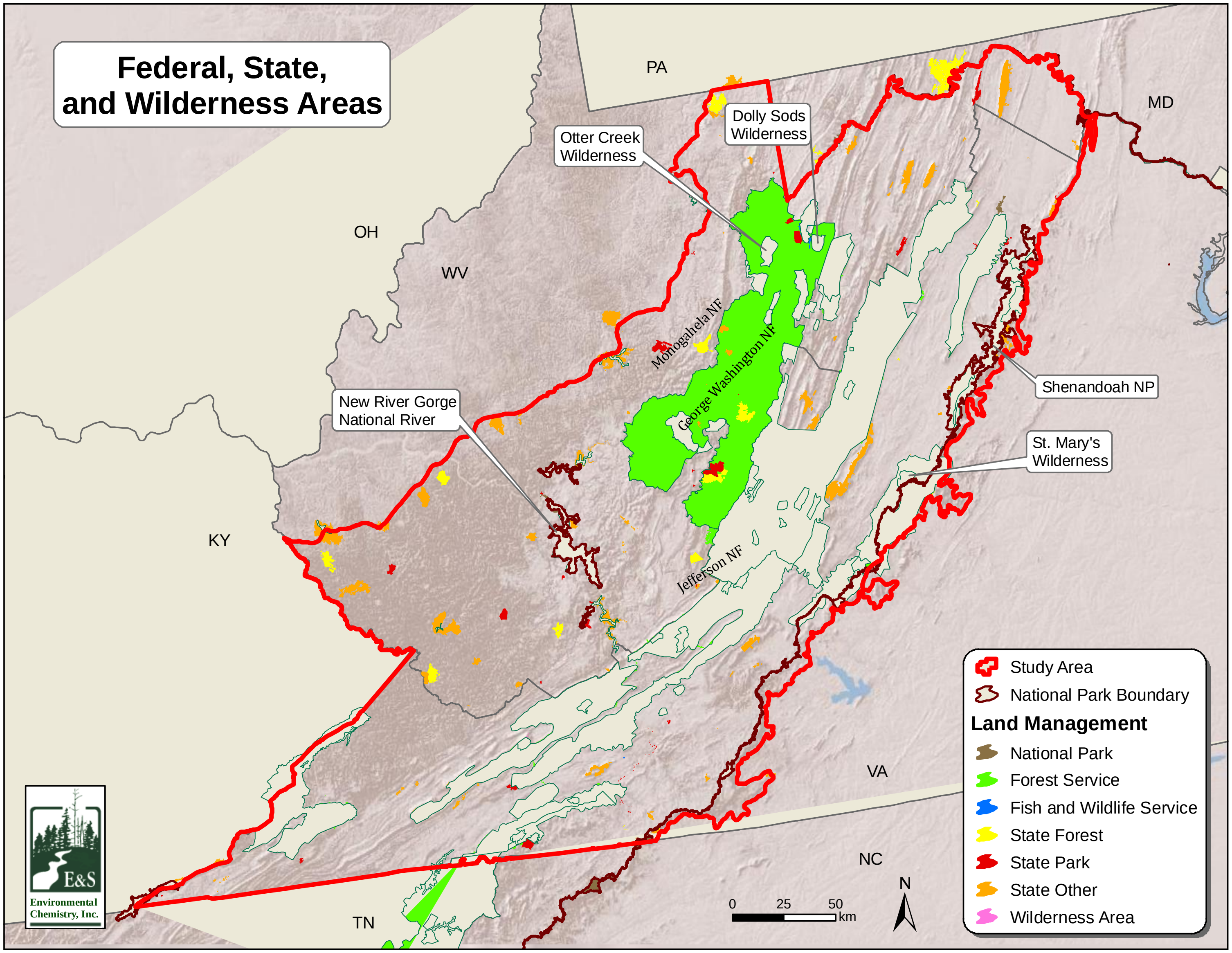


Figure 3. Map showing federal and state lands within the study area. Wilderness area boundaries are also shown.

A subset of these streams (n=100) was selected for dynamic modeling, including streams within the study region for which MAGIC model calibrations had previously been constructed. A geographic information system (GIS) data set was compiled for the study region that depicted regional spatial coverages of geologic sensitivity classes, soils characteristics, elevation, and watershed morphology (area, average slope).

2.2 Modeling

2.2.1 Steady State Water Chemistry Model

A modified version of the SSWC model (Sverdrup et al. 1990, Henriksen et al. 1992, Henriksen and Posch 2001) was used to calculate the steady state CL of acidity (CL(A)) for surface waters. It is based on the principle that acid loads should not exceed the balance of non-marine, non-anthropogenic base cation sources and sinks in a watershed, minus a buffer to protect selected aquatic biota from being damaged. This study employs the SSWC model as given in Equation 1 and also includes the necessary terms associated with biological N removal and immobilization. Nitrogen can be removed from the soil via uptake by tree boles that are harvested and removed from the watershed (N_{up}) and also through microbial denitrification (N_{de}) and long-term nitrogen immobilization (N_i) in forest soils. The CL of acidity is therefore calculated for this study as:

$$CL(A) = BC_{dep} + BC_w + N_{up} + N_{de} + N_i - Bc_{up} - ANC_{limit} \qquad (2)$$

where N_{de} is the removal of N from the site by denitrification, N_i is the immobilization of N by microbes, and N_{up} is the forest uptake of N. Note that the three N sink terms in this equation are included in addition to the CL equation parameters described by Henriksen and Posch (2001) for the SSWC. The addition of these terms renders Equation 2 similar in form to the First-order Mass Balance (FAB) model also used to calculate aquatic CL's (cf. Henriksen and Posch, 2001), the difference here being that the N terms in Equation 2 were estimated from regional empirical data rather than calculated based on landscape characteristics.

Because each of the variables given in Equation 1 can be estimated at broad spatial scales, it is possible to use the SSWC model to develop regional estimates of CL and CL exceedances. This model function allows assessment of regional patterns in acidification

sensitivity and effects. It also allows for calculation of the total stream length and percent of stream length within the region of interest that fall within certain CL or exceedance classes.

All CL values calculated and presented in this report are based on the steady state approach given in Equation 2, and are expressed as CL(A), critical loads of acidity. These loads include both S and N sources of acidity.

2.2.2 MAGIC Model

MAGIC is a lumped-parameter model of intermediate complexity, developed to predict the long-term effects of acidic deposition on surface water chemistry (Cosby et al. 1985). The model simulates soil solution chemistry and surface water chemistry to predict the monthly and annual average concentrations of the major ions in these waters. MAGIC consists of: 1) a section in which the concentrations of major ions are assumed to be governed by simultaneous reactions involving SO_4^{2-} adsorption, cation exchange, dissolution-precipitation- speciation of Al and dissolution-speciation of inorganic C; and 2) a mass balance section in which the flux of major ions to and from the soil is assumed to be controlled by atmospheric inputs, chemical weathering, net uptake and loss in biomass and loss to runoff. At the heart of MAGIC is the size of the pool of exchangeable base cations in the soil. As the fluxes to and from this pool change over time owing to changes in atmospheric deposition, the chemical equilibria between soil and soil solution shift to give changes in surface water chemistry. The degree and rate of change of surface water acidity thus depend both on flux factors and the inherent characteristics of the affected soils.

Cation exchange is modeled using equilibrium (Gaines-Thomas) equations with selectivity coefficients for each base cation and Al. Sulfate adsorption is represented by a Langmuir isotherm. Aluminum dissolution and precipitation are assumed to be controlled by equilibrium with a solid phase of $Al(OH)_3$. Aluminum speciation is calculated by considering hydrolysis reactions as well as complexation with SO_4^{2-} and fluoride. Effects of carbon dioxide on pH and on the speciation of inorganic carbon are computed from equilibrium equations. Organic acids are represented in the model as tri-protic analogues. First-order rates are used for biological retention (uptake) of NO_3^- and ammonium in the soils and streams. Weathering of base cations is determined as part of the calibration process and is assumed to be constant. In the application here, nitrogen uptake dynamics do not vary in the long term. A set of mass balance equations for base cations and strong acid anions are included.

Given a description of the historical deposition at a site, the model equations are solved numerically to give long-term reconstructions of surface water chemistry (Cosby et al. 1989). MAGIC has been used to reconstruct the history of acidification and to simulate future trends on a regional basis and in a large number of individual catchments in both North America and Europe (e.g., Lepisto et al. 1988; Whitehead et al. 1988; Cosby et al. 1989, 1990, 1996; Hornberger et al. 1989; Jenkins et al. 1990a-c; Wright et al. 1990, 1994; Norton et al. 1992; Sullivan and Cosby 1998).

MAGIC Calibration Protocol

The aggregated nature of MAGIC requires that it be calibrated to observed data from a system before it can be used to examine potential system response. Calibration is achieved by setting the values of certain parameters within the model that can be directly measured or observed in the system of interest (called fixed parameters). The model is then run (using observed and/or assumed atmospheric and hydrologic inputs) and the outputs (streamwater and soil chemical variables - called criterion variables) are compared to observed values of these variables. If the observed and simulated values differ, the values of another set of parameters in the model (called optimized parameters) are adjusted to improve the fit. After a number of iterations adjusting the optimized parameters, the simulated-minus-observed values of the criterion variables usually converge to zero (within some specified tolerance). The model is then considered calibrated.

There are eight parameters to be optimized in this procedure (the weathering and the selectivity coefficient of each of the four base cations), and there are eight observations that are used to drive the estimate (current soil exchangeable pool size and current output flux of each of the four base cations). If new assumptions or new values for any of the fixed variables or inputs to the model are adopted, the model must be re-calibrated by re-adjusting the optimized parameters until the simulated-minus-observed values of the criterion variables again fall within the specified tolerance.

Estimates of the fixed parameters, deposition inputs, and the target variable values to which the model is calibrated all contain uncertainties. A “fuzzy optimization” procedure was utilized in this project to provide explicit estimates of the effects of these uncertainties. The procedure consists of multiple calibrations at each site using random values of the fixed parameters drawn from a *range* of fixed parameter values (representing uncertainty in knowledge

of these parameters), and random values of Reference Year deposition drawn from a *range* of total deposition estimates (representing uncertainty in these inputs). The final convergence (completion) of the calibration is determined when the simulated values of the criterion variables are within a specified "acceptable window" around the nominal observed value. This "acceptable window" represents uncertainty in the target variable values being used to calibrate the site.

Each of the multiple calibrations at a site begins with (1) a random selection of values of fixed parameters and deposition, and (2) a random selection of the starting values of the adjustable parameters. The adjustable parameters are then optimized using an algorithm seeking to minimize errors between simulated and observed criterion variables. Calibration success is judged when all criterion values simultaneously are within their specified "acceptable windows", which may occur before the absolute possible minimum error is achieved. This procedure is repeated 10 times for each site.

For this project, the acceptable windows for base cation concentrations in streams were taken as +/- 2 μeq/L around the observed values (+/- 5 μeq/L for Ca^{2+}). Acceptable windows for soil exchangeable base cations were taken as +/- 0.2% around the observed values (+/- 0.5% for Ca^{2+}). Fixed parameter uncertainty in soil depth, bulk density, cation exchange capacity, stream discharge, and stream area were assumed to be +/- 10% of the estimated values. Uncertainty in total deposition was +/- 10% for all ions.

The final calibrated model at each site is represented by the ensemble of parameter values of all of the successful calibrations at the site. When performing simulations at a site, all of the calibrated parameter sets in the ensemble are run for a given historical or future scenario. The result is multiple simulated values of each variable in each year, all of which are acceptable in the sense of the calibration constraints applied in the fuzzy optimization procedure. The median of all the simulated values within a year is the "most likely" response for the site in that year. For this project, whenever single values for a site are presented or used in an analysis, these values are the median values derived from running all of the ensemble parameter sets for the site.

<u>MAGIC Weathering Estimates</u>

MAGIC is an aggregated catchment model. The base cation weathering terms in MAGIC are intended to represent the catchment-average weathering rates for the soil compartments. In a one soil-layer application of MAGIC (such as here) the weathering rates in MAGIC thus reflect the catchment-average net supply of base cations to the surface waters draining the catchment.

The sum of the MAGIC weathering rates for the individual base cations is therefore identical in concept to the base cation weathering term, BC_w, in the SSWC CL model. Base cation weathering rates from MAGIC should be directly applicable in the SSWC model.

Base cation weathering rates in MAGIC are calibrated parameters. The calibration procedure uses observed deposition of base cations, observed (or estimated) base cation uptake in soils, observed stream water base cation concentrations, and runoff. These observed input and output data provide upper and lower limits for internal sources of base cations in the catchment soils. The two most important internal sources of base cations in catchment soils are modeled explicitly by MAGIC: primary mineral weathering and soil cation exchange. During the calibration process, observed soil base saturation for each base cation and observed soil chemical characteristics are combined with the observed input and output data to partition the inferred net internal sources of base cations between weathering and base cation exchange.

Weathering is assumed constant in MAGIC, but base cation exchange varies through time as anion fluxes change and as the soil base saturation increases or decreases. Therefore, the calibration simulations are performed over an historical period of approximately 150 years. Weathering and cation exchange selectivity coefficients are selected during calibration such that the model starts with “reasonable” soil and stream conditions, responds to the 150 year period of deposition changes at the site, and ends with simulated values of stream and soil base cations that are consistent with the currently observed stream export at the site and the current observed soil base saturation at the site. The partitioning of observed base cation export into weathering and cation exchange by MAGIC is thus heavily constrained by observed deposition, soil and stream water data. The better the data quality, the more extensive the soils measurements, the longer the observed record, the more robust and reliable the weathering estimates are likely to be.

The catchment-average estimates of weathering rates derived from MAGIC calibrations provide data-constrained, site-specific, conceptually appropriate values for inclusion in the SSWC model for that site. The calibrated MAGIC weathering estimates at multiple sites in a region can be used as the basis for development of empirical regression models to spatially extrapolate the site-specific weathering rates to the regional landscape.

Calibration of MAGIC to Study Sites

For each of the 100 selected study sites, the MAGIC model calibrations conducted as part of the previously completed Southern Appalachian Mountain Initiative (SAMI) modeling project

(Sullivan et al. 2002), Shenandoah Park Assessment (Sullivan et al. 2003), and Monongahela National Forest modeling effort (Sullivan and Cosby 2004) were retrieved. These already developed model calibrations provided the starting point for the MAGIC re-calibrations in this project. Details of the original input databases, data aggregation procedures, and protocols for assigning wet and dry deposition, soils and streamwater inputs for MAGIC at each site are given by Sullivan et al. (2002, 2004).

Some changes in the original SAMI model calibration protocols were required for this project because the base cation weathering values derived from the MAGIC calibrations were passed directly to the SSWC model for individual site estimations of CLs (or extrapolated to a GIS layer for later spatial estimation of SSWC CLs). It was therefore important that all assumptions or inputs being used for the SSWC model also be included in the MAGIC calibrations. To bring the original SAMI calibrations of MAGIC in line with the assumptions being used to implement the SSWC CLs model for this project, three components employed in the calibration approach used for the SAMI aquatic assessment (Sullivan et al. 2002) were changed. With the exception of these three components (described below), all other inputs to MAGIC were identical to those used in the original SAMI project.

First, the dry deposition of base cations and chloride (Cl^-) were modified slightly from the original SAMI values. This was necessary to make the total deposition of base cations and Cl^- used for MAGIC calibrations equal to the total deposition of those ions to be used in the SSWC model calculations.

Second, during the original SAMI calibrations, an examination of the empirical input-output mass balances of SO_4^{2-} and Cl^- for each of the sites revealed slight discrepancies at some of the sites. For those sites, the estimated stream outputs of these ions were higher than the estimates of deposition inputs. As a result, small catchment sources of SO_4^{2-} and Cl^- were assumed during the MAGIC calibrations for SAMI. The values of those catchment sources were re-derived for this project to bring the mass balances into alignment with the more recent deposition data to be used in the SSWC model. Of the sites included in this study, 16 were simulated as having small sources of SO_4^{2-} and Cl^- in their catchments.

Third, assumptions regarding internal soil sources and sinks were modified from the original SAMI protocol. In the SAMI study, the base cation uptake from soils by forest growth and harvesting was not included in the MAGIC calibrations. Because the SSWC explicitly

includes these terms, it was necessary to include them as soil sinks of base cations in the re-calibrations of MAGIC for this project.

Following the three adjustments to the input data described above, the 100 sites were re-calibrated using the "fuzzy" optimization procedure. For 92 of the sites, the optimization procedure produced 3 or more successful calibrations out of the 10 attempted for the site (85 of the sites had 7 or more successful calibrations). The median simulated values (of the ensemble of successful calibrations) at each of the 92 sites agree well with the observed data during the calibration year (Figure 4). The median weathering estimates extracted from the MAGIC calibrations for these 92 sites were used in the next phase of this study.

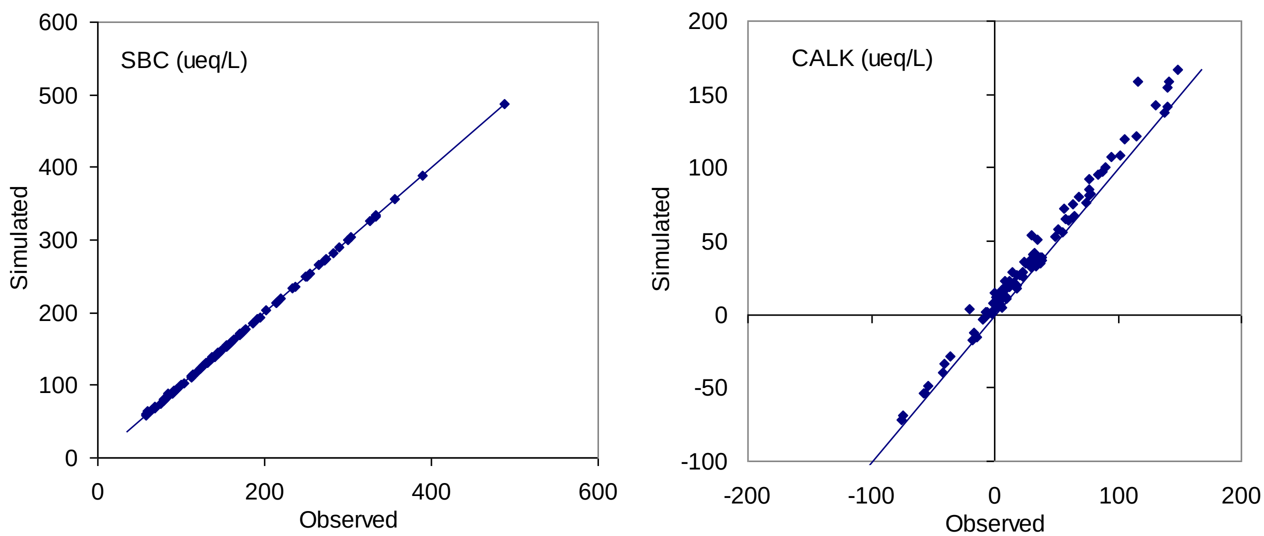


Figure 4. Simulated vs observed values of sum of base cations and calculated ANC (CALK) for the calibration period at each of the study sites modeled using MAGIC (n = 92).

2.3 Regional Extrapolation of Base Cation Weathering for Input to SSWC

Calibrated MAGIC estimates of effective base cation weathering (BC_w) at individual modeling sites were extrapolated to the study region using a combination of water chemistry and/or landscape variables thought or known to be associated with weathering rates and watershed acid sensitivity. The candidate independent variables are described below. The major steps employed in developing regional estimates of BC_w were as follows:

1. Identify candidate stream sites for dynamic modeling.

2. Refine MAGIC model calibrations and extract effective watershed-specific BC_w estimates for the dynamic modeling sites.
3. Compile regional data on stream chemistry and candidate explanatory landscape variables for extrapolation of the weathering estimates derived for the dynamic modeling sites to the regional landscape.
4. Develop an approach for watershed delineation in the regional landscape.
5. Develop empirical relationships with which to extrapolate BC_w to the study region, using regional stream chemistry and/or landscape characteristics.
6. Process predictor variable data using grid cell flow direction derived from the digital elevation model (DEM) and a continuous upslope averaging model.
7. Calculate BC_w for each 30-m pixel within the study area using the empirical relationships that were established in Step 5 and the upslope continuously averaged predictor variable datasets calculated in Step 6.

2.3.1 Input Data for BC_w Regression Equations

Stream Chemistry

The acid-base chemistry of streams is reflected in the stream water by ANC and the concentrations of strong mineral acid anions and base cations in solution. Thus, candidate water chemistry independent variables selected for this analysis included the variables given in Table 1. MAGIC calculates ANC as the difference between the sum of the base cations (SBC) and the sum of the mineral acid anions (SAA). The calculated ANC is termed CALK.

Elevation and Slope

Elevation data at a resolution of one arc-second (approximately 30 m) were extracted from the U.S. Geological Survey (USGS) National Elevation Dataset. Average elevation and percent slope for each watershed modeled with MAGIC were calculated from the elevation data.

Geologic Sensitivity

Data representing regional geologic sensitivity were mapped at coarse resolution (1:250,000 scale) based on USGS lithology data (Sullivan et al. 2007). The geologic sensitivity classes represented by the data included siliciclastic, argillaceous, felsic, mafic, and carbonate.

Table 1. Candidate variables for predicting BC_w.

Landscape Characteristics	Water Chemistry
• Watershed area	• Sum of base cations
• Elevation	• Sum of base cations – chloride
• Slope	• Calculated ANC
• % siliciclastic	• Sulfate
• % argillaceous	• Nitrate
• % felsic	
• % mafic	
• % carbonate	
• % clay in soil	
• Soil pH	
• Soil depth to restricting layer	

The polygon data were converted to five grids, each representing an individual sensitivity class. Grid cells were assigned a value of 1 to indicate presence of the respective sensitivity class and 0 representing its absence. A weighted-average kernel smoother was used to generate a transition zone of approximately 800 m between adjacent geologic sensitivity classes to reflect the coarse scale and spatial uncertainty in the lithology data.

Soils

Soils data from the Soil Survey Geographic (SSURGO) database were available for the majority of the study area (http://soils.usda.gov/survey/geography/ssurgo/). Where SSURGO data were not available, the coarser-scaled State Soil Geographic (STATSGO2; U.S. General Soils Map, http://soils.usda.gov/survey/geography/statsgo/) data were substituted. Soil parameters that were extracted from these databases for this study included depth to restricting layer, percent clay, and pH. SSURGO and STATSGO2 are spatially represented using “map units”. Each map unit is typically comprised of multiple “components”. The soils parameters were tabulated and coded to each soil map unit based on a component weighted average. The resulting tabular data were joined with the spatial polygon data and converted to a 30-m grid using the maximum area cell assignment option in ArcGIS.

Depth to restricting layer was defined as the depth to the first layer that prevents root penetration and water movement as represented in the soil databases. These depths were calculated for each component and then weighted and summed to generate a representative depth

to restricting layer for each map unit. STATSGO2 data were used where SSURGO data contained no data or a value of 0. A limited portion of the study area was classified as open water, and was represented in SSURGO as having no soils data. The no-data cells (corresponding with open water) were filled with an average of the nearby data cells (30 x 30 cell window) using the focal statistics function in ArcGIS. This step was required in order to maintain continuity during application of the continuous upslope averaging function.

Soil components in SSURGO and STATSGO2 are attributed with percent clay at multiple soil horizons. Therefore, percent clay was calculated as a soil horizon thickness weighted average for each component. The representative percent clay for each map unit was then calculated as a component weighted average. STATSGO2 data were used where SSURGO data contained no-data or a value of 0. The open water cells were treated as for soil depth calculations. The same methods as described for percent clay were followed for generating a representative pH value for each map unit.

2.3.2 Establishing BC_w Predictor Equations

Regression input data were developed at different scales, ranging from 30-m DEM grid data to lithologic polygon data developed at a scale of 1:250,000 in West Virginia and 1:500,000 in Virginia (Table 2). In order to use a regression approach to estimate BC_w from calibrated MAGIC BC_w, it was necessary to express all candidate predictor variables on a grid basis at the same scale. This was accomplished at the 30-m grid scale, which provided sufficient resolution to conduct flowpath analyses that could be used to develop topographically determined streams. Polygon data were resampled to 30-m grid cells, preserving the data developed at the original

Table 2. Source and scale of input data for spatial extrapolation.

Dataset	Source	Scale or Resolution
Elevation	National Elevation Dataset (NED)	1 arc-second (30m)*
Slope	Derived from NED data	1 arc-second (30m)*
Geology	USGS Statewide Geology	1:250,000 (WV), 1:500,000 (VA)
Soils	SSURGO STATSGO	1:24,000 1:250,000
Watershed Area	Derived from NED data	1 arc-second (30m)*

* approximately equivalent to 1:24,000

input database scale. The only scale adjustment that was made involved generating a transition zone between adjacent geologic sensitivity classes to smooth out the uncertainty in the geologic sensitivity class boundary locations.

Regression techniques were used to establish equations to be used for BC_w prediction within each of the three study ecoregions. MAGIC model estimates of BC_w for the 92 calibrated watersheds located throughout the study area were used as observed weathering rates. Both landscape and water chemistry variables were used as predictor variables in the regression analyses (Table 1).

Each of the calibrated MAGIC study watersheds was placed in an ecoregion category based on which ecoregion contained the maximum watershed area. Two predictor equations were established for each of the three ecoregions, one using both landscape characteristics and water chemistry parameters (for use in watersheds for which stream chemistry data are available) and another using landscape characteristics only. Watershed averages were used to represent the spatial variability within each watershed for the landscape characteristics, except for watershed area.

Regression models were established using stepwise linear regression in Statistix 8.0. Best subset regression was used for model selection in the Blue Ridge ecoregion using landscape variables only, in order to reduce the number of independent predictor variables. Regional distributions of the candidate predictor variables are described for each study ecoregion in Appendix B.

2.3.3 BC_w Estimates for Sites with Water Chemistry, Based on Water Chemistry plus Landscape Variables

Water quality predictor data had been collected during several regional surveys, as compiled by Sullivan et al. (2002) and Sullivan and Cosby (2004). One water quality sample, generally collected during the spring between 1985 and 2001, was used to characterize each watershed. Water quality data were derived from several regional surveys, including the National Stream Survey (NSS), Environmental Monitoring and Assessment Program (EMAP), Virginia Trout Stream Sensitivity Study (VTSSS), and stream surveys conducted in Monongahela National Forest (cf., Sullivan and Cosby 2004). Watershed averages of the landscape predictor variables were calculated using the zonal statistics function in ArcGIS. Estimates of BC_w were

made using the appropriate regression equation as established through the methods described below. Coefficients and their standard errors are given in Appendix C.

2.3.4 BC_w Estimates for Entire Study Area, Based on Landscape Variables Only

Continuous upslope averages for each of the landscape predictor variables were calculated for each 30-m grid cell using hydrologically conditioned DEM data derivatives (NHDPlus). The continuous upslope averaging function begins with using a continuous spatial dataset (such as soil pH) as a weighting factor in a DEM-based flow accumulation algorithm within ArcGIS (Jenson and Domingue 1988, Verdin and Worstell 2008). This function sums all of the data values that occur within cells upslope from the target cell. This accumulated data layer is then added to the raw input data layer in order to account for the value that occurs at the target cell itself. A value of one is added to the flow accumulation grid, which results in a count of all upstream contributing cells including the target cell. These two values are then divided to generate an average of all data values that occur upslope from the target cell. This process is described by the equation:

$$P_{avg} = (P + P_{fac})/(fac + 1) \tag{3}$$

where P_{avg} = upslope averaged parameter value
P = a continuous input parameter
P_{fac} = a flow accumulated input parameter
fac = flow accumulation grid

Each of the input landscape datasets was processed in this manner, except for watershed area. Watershed area was obtained by summing the new contributing area gained while moving down gradient (i.e., setting the denominator in the above equation equal to 1).

Stream chemistry input data for the regression models were the same as the stream data used to calibrate MAGIC. However, none of the landscape variables listed in Table 1 were used in calibrating MAGIC. Thus, the extrapolations based only on landscape variables, which were used for the regional CL evaluation, were independent of any calculations done with MAGIC.

2.4 Calculation of Critical Loads and Exceedances

2.4.1 Inputs for SSWC Critical Load Calculations

<u>BC Weathering</u>

Base cation weathering values for the SSWC were derived from regional extrapolations of weathering estimates extracted from the MAGIC model calibrated to 92 sites in the study region (see section 2.3). Two extrapolation methods were employed which allowed estimation of BC_w at any location in the study region using either landscape characteristics and observed stream water chemistry, or landscape characteristics alone.

<u>BC Deposition</u>

Wet deposition estimates were obtained from interpolated National Acid Deposition Program (NADP) data at 375 m resolution. A five-year average centered on 2002 was used as model input. Literature values of dry:wet deposition ratios for the Southern Blue Ridge Mountains were used to estimate dry deposition of base cations from the NADP interpolations (Baker et al. 1991). BC_{dep} was corrected for sea-salt influence by subtracting the Cl^- deposition rate. Total deposition may be underestimated at the highest elevation areas, where unmeasured cloud deposition might be quantitatively important. BC_{dep} was calculated as a continuous upslope average, using the procedures developed for calculation of BC_w.

<u>Nitrogen Immobilization and Denitrification</u>

Denitrification rates in boreal and temperate ecosystems can be variable. Denitrification was set to 7.14 meq/m^2/yr (1 kg N/ha/yr) as an approximate average representative value for the study area (cf., Ashby et al. 1998). Long-term net nitrogen immobilization (N_i) was set to 4.3 meq/m^2/yr (McNulty et al. 2007).

<u>ANC Limit</u>

The ANC_{limit} was calculated for the various CL applications as the product of estimated runoff and the designated critical ANC criteria values (0, 20, 50, 100 μeq/L). These ANC thresholds for biological response should be interpreted within the context of known or suspected dose-response functions, summarized for Shenandoah National Park in Appendix A. They should also be interpreted within the context of model hindcast estimates of pre-industrial stream chemistry, which are given for the 92 MAGIC sites in Appendix D.

While the ANC criteria values did not vary across the study region, the runoff used to calculate the ANC_{limit} was assumed to vary spatially. An algorithm was developed using USGS runoff estimates at gaging stations within the study region, combined with elevation and orographically-correlated precipitation amounts from the Parameter-elevation Regressions on Independent Slopes Model (PRISM) , to estimate fine-scale variation in runoff across the study domain (Figure 5). The ANC limit was not calculated as an upslope average using the watershed pixels because the runoff term used to calculate the ANC_{limit} already reflects an upslope averaged condition.

Forest Uptake

Forest uptake fluxes of the three nutrient base cations (Ca^{2+}, Mg^{2+}, K^{+}; Bc_{up}) and nitrogen (N_{up}) were estimated from literature values summarized from the U.S Forest Service, Forest Inventory Analysis (FIA) project by McNulty et al. (2007). It was assumed that 65% of the estimated average forest volume increment is removed from the watershed annually through

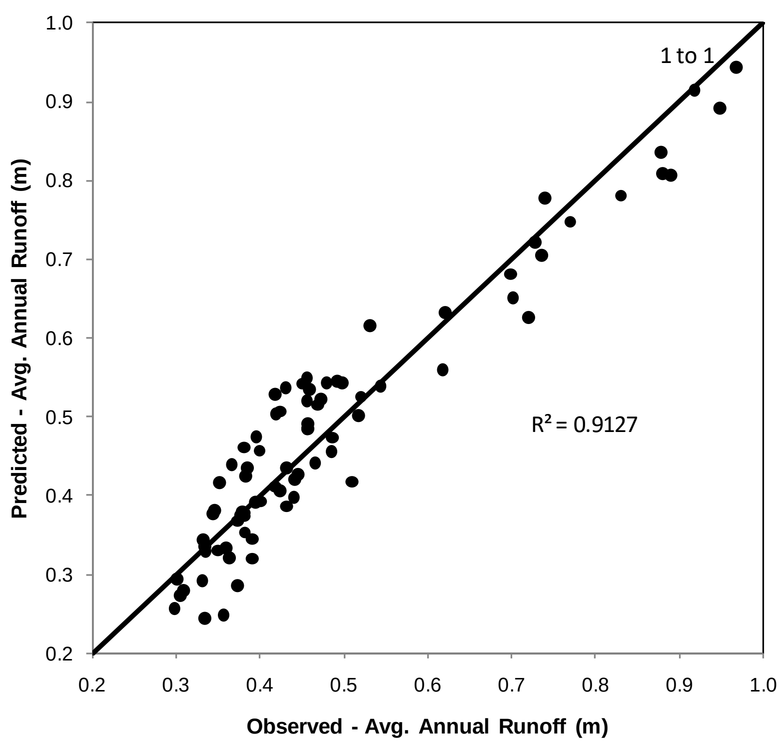


Figure 5. Predicted (from PRISM precipitation model and elevation) versus observed (at USGS gages) runoff in Virginia and West Virginia. The predictive equation was used to predict runoff for the study region. Predictions beyond the range of observed values were truncated at the levels of the extreme values.

harvesting. These uptake terms reflect uptake into woody materials that are removed from the watershed through forestry practices. Uptake into vegetation that subsequently dies on site represents within-watershed recycling; this is not a watershed output and is not included in the SSWC model calculations. Lands identified as national park, designated Wilderness, and other protected areas were classified as "no harvest"; Bc_{up} and N_{up} were set to zero in such areas. These areas included the Protected Areas database constructed by the Commission for Environmental Cooperation, corresponding to GAP codes 1 and 2 (Scott et al. 1993). It must be recognized that other forest lands, for example in the national forests, may also be considered "no harvest" under current, or future, management plans. The possible existence of such management policies is not accounted for in the modeling reported here. Bc_{up} and N_{up} were calculated as continuous upslope averages, using the procedures developed for calculation of BC_w.

2.5 Critical Load and Exceedance Calculation Methods

Each of the terms in the SSWC model was calculated for every 30-m grid cell in the study region and then combined to yield an estimate of CL for each grid cell. Each of the variables in the SSWC formulation (Equation 2) was represented as a spatial coverage across the study region based on the topographically determined watershed polygons. The CL values for each threshold ANC value were calculated and mapped. Watershed CL values were then extracted with the topographically derived stream network to include only those 30 m pixels that occurred along the stream grid cells. Results of the CL calculations for those pixels that occurred along topographically derived streams were averaged to yield the CL of the stream reach that flowed through each watershed. These watershed CL estimates were intersected with the high-resolution NHD dataset to yield a regional coverage of stream reaches, coded by CL class.

Critical load and ambient deposition acidity data were overlayed to determine the exceedance, or the amount by which ambient deposition exceeds the estimated CL. Exceedance maps were developed for the various threshold ANC values.

Atmospheric deposition of acidity, CL(A), and exceedances at the various ANC threshold values are all reported and mapped in equivalents per unit watershed area, rather than for example in kilograms per hectare or some other mass unit basis. This is necessary in order to combine S acidity and N acidity to evaluate total deposition acidity. For a given amount of

deposition acidity, there exists an infinite number of possible combinations of S and N inputs that could achieve that acidity. However, in most watersheds within the study region, mineral acid anion leaching is comprised primarily by SO_4^{2-}; in general, most atmospheric N is retained in watershed soils and vegetation, with limited NO_3^- leaching (Sullivan et al. 2002). Therefore, equivalent units of deposition can be approximately converted to mass units if one makes assumptions about the contribution of N to the acidity of deposition. For example, if all of the acidity is derived from S, and none is derived from N, then CL(A) in units of meq/m^2/yr times 0.16 is equal to CL of S deposition in units of kg S/ha/yr.

3.0 RESULTS

3.1 MAGIC Simulations and Development of Equations to Predict BC_w

A total of 92 stream sites were successfully calibrated using MAGIC. BC_w estimates for those watersheds were extracted from the calibration files. Of those sites, 26 were in the Blue Ridge, 42 in the Ridge and Valley, and 24 in the Central Appalachian ecoregion. Ecoregion-specific regression equations were developed with which to predict the MAGIC estimates of BC_w at the 92 sites. Two sets of predictive equations were developed, using either stream chemistry and watershed features (for 522 sites for which water chemistry data had been compiled) or using watershed features alone (for all watersheds within the study area). The predictor water chemistry variables included calculated ANC, sum of base cations, and NO_3^- concentration. Significant predictor landscape variables included aspects of lithology (% siliciclastic, felsic, mafic, or carbonate geological types), soils characteristics (pH, depth to confining layer, % clay), and watershed physical condition (area, elevation, average slope; Table 3). For the predictive equations that included water chemistry, neither the soils variables nor the geologic variables were included in the final regression equations. In contrast, for the predictive equations that did not include water chemistry, one or more soil variables were included and for

two of the three ecoregions one or more geologic variables were included in the final regression equations. This result is likely because stream chemistry integrates soil and geologic condition within the watershed, and may be a better predictor of catchment weathering than available aggregated and mapped soil and geologic information. Thus, geologic and edaphic variables do not provide much additional explanatory power if water chemistry data are already included in the regression relationship.

Table 3. Multiple regression equations to estimate BC_w from either water chemistry and landscape variables or from landscape variables alone, stratified by ecoregion.

Ecoregion	n	Equation[1]	r^2
Water Chemistry and Landscape Variables			
Central Appalachian	24	$BC_w = -37.5 + 0.6\ (SBC) + 0.9\ (NO_3) + 0.006\ (WS\ Area)$	0.93
Ridge and Valley	42	$BCw = 107.0 + 0.5\ (SBC) - 0.06\ (Elevation) - 3.2\ (Slope)$	0.86
Blue Ridge	26	$BC_w = 27.1 + 0.6\ (CALK) + 0.6\ (NO_3)$	0.90
Landscape Variables Only			
Central Appalachian	24	$BC_w = 1186.2 + 0.01\ (WS\ Area) – 0.3\ (Elevation) – 179.3\ (Soil\ pH)$	0.66
Ridge and Valley	42	$BC_w = 219.7 - 74.6\ (\%\ Siliciclastic) + 6632.4\ (\%\ Carbonate) – 0.1\ (Elevation)$	0.64
Blue Ridge	26	$BC_w = 57.9 + 32.7\ (\%\ Felsic) + 69.6\ (\%\ Mafic) - 40.2\ (Soil\ Depth) + 2.0\ (Soil\ \%\ Clay)$	0.85

[1] SBC is sum of base cations; CALK is calculated ANC.

Watershed boundaries and stream sampling locations for the MAGIC sites are shown in Figure 6. Most modeled watersheds are small and located at moderate to high elevation (Figure 7). Few sites were below 500 m elevation. Percent watershed slope was variable, with most sites having slope greater than about 10% (Figure 8). Much of the geology in the study area is expected to exhibit relatively low weathering rates, based on the preponderance of siliciclastic and argillaceous lithologies (Figure 9; cf., Sullivan et al. 2007). Soil % clay is relatively high (greater than about 15%) throughout much of the study area (Figure 10), with nearly all areas having % clay above 10%. Soil pH typically varied between about 4.5 and 5.5 (Figure 11). Soils are generally shallow (less than about 1 m to a confining layer in large portions of the study areas), but deeper soils are also common (Figure 12).

Equations for the three ecoregions with which to predict BC_w, using a combination of stream chemistry and watershed features, yielded good agreement with MAGIC simulations of catchment weathering (Figure 13; Table 3). For the Blue Ridge ecoregion, the predictive equation based on landscape data alone (% felsic and mafic lithologies, soil % clay, soil depth) explained nearly as much of the variation in MAGIC weathering (85%) as the equation based on water chemistry (calculated ANC and stream NO_3^- concentration); none of the landscape variables entered into that equation (Table 3). For the Ridge and Valley and the Central Appalachian ecoregions, the equations to predict BC_w based on landscape variables alone

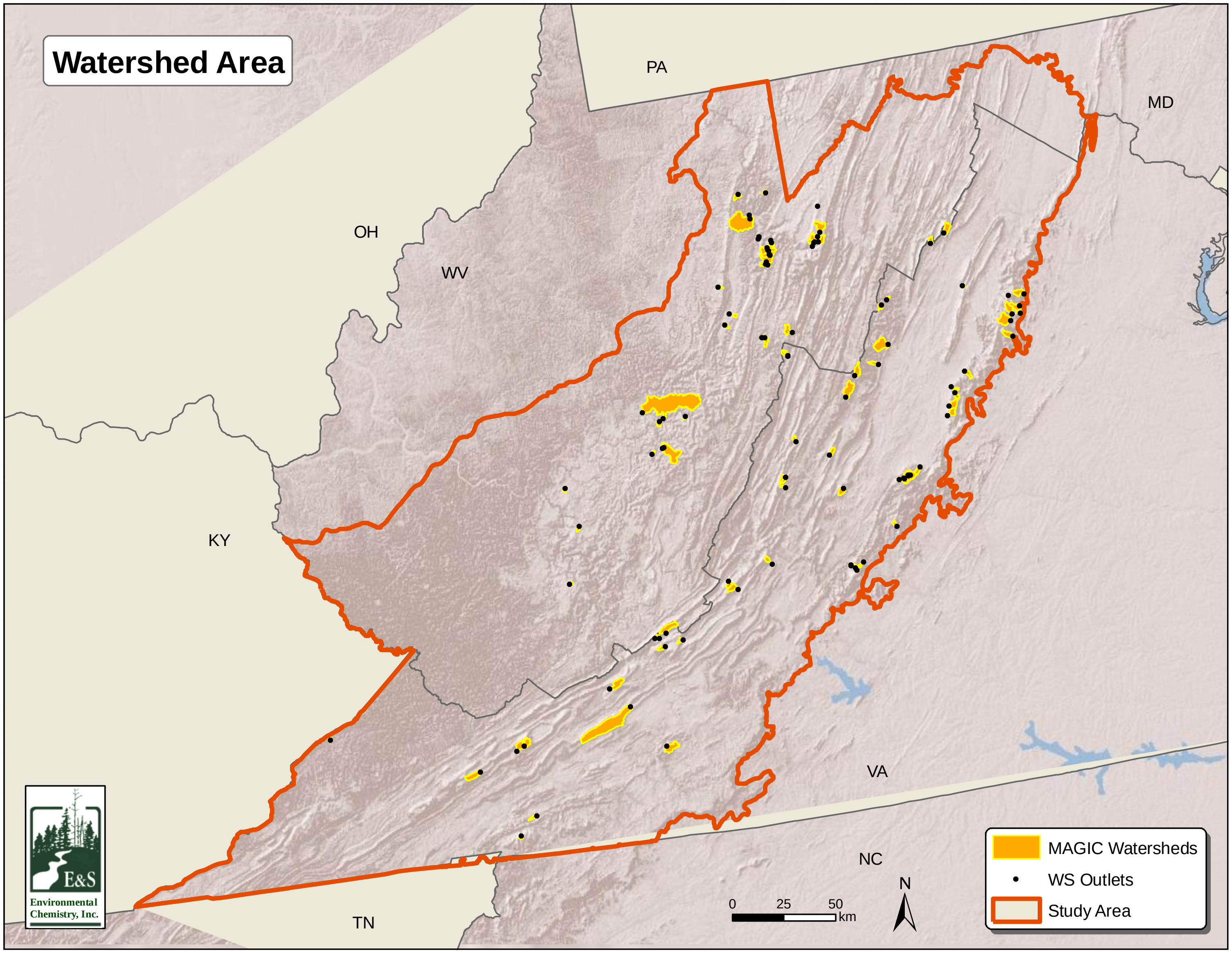


Figure 6. Stream sampling locations and associated watersheds for sites modeled with MAGIC.

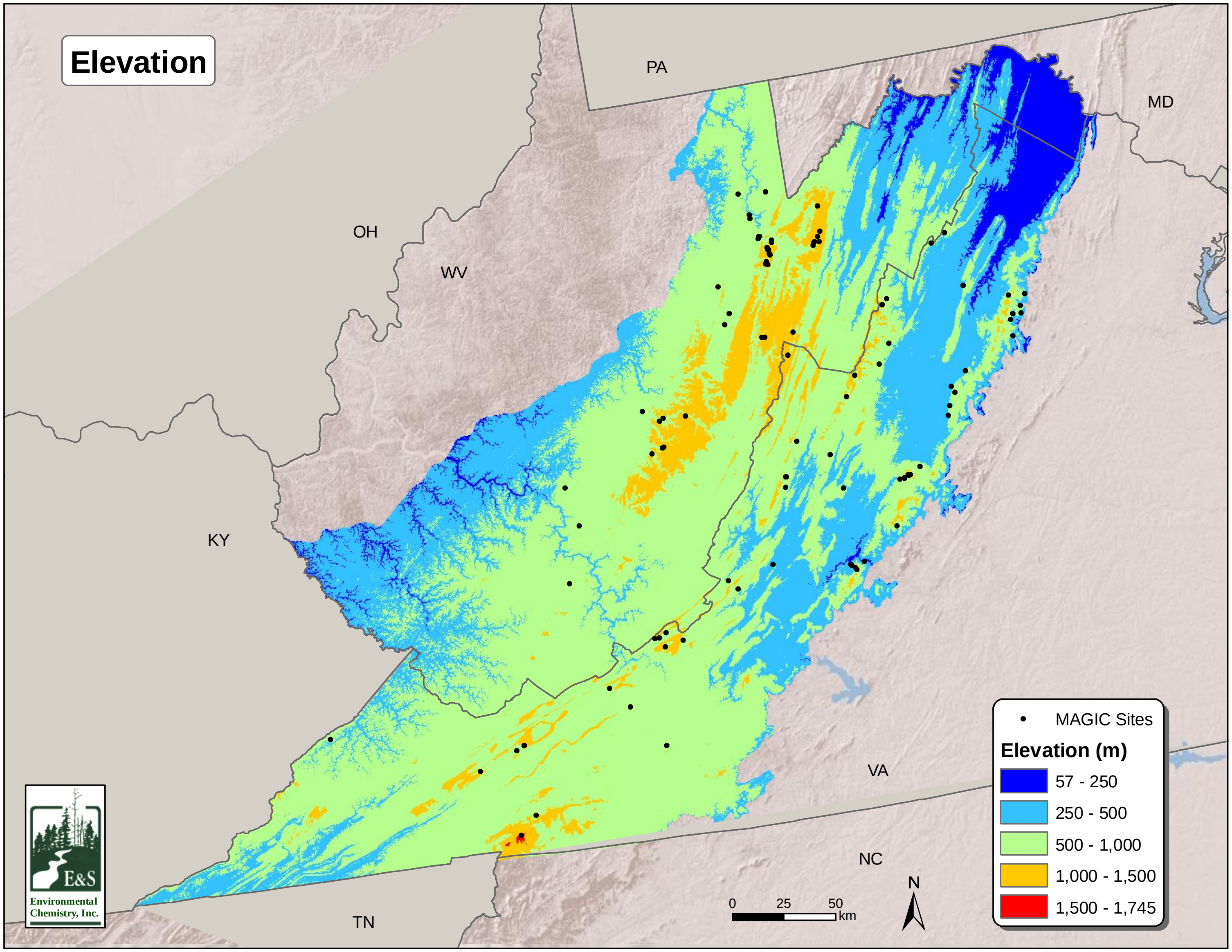


Figure 7. Elevation pattern across the study area. Also shown are MAGIC model sampling sites.

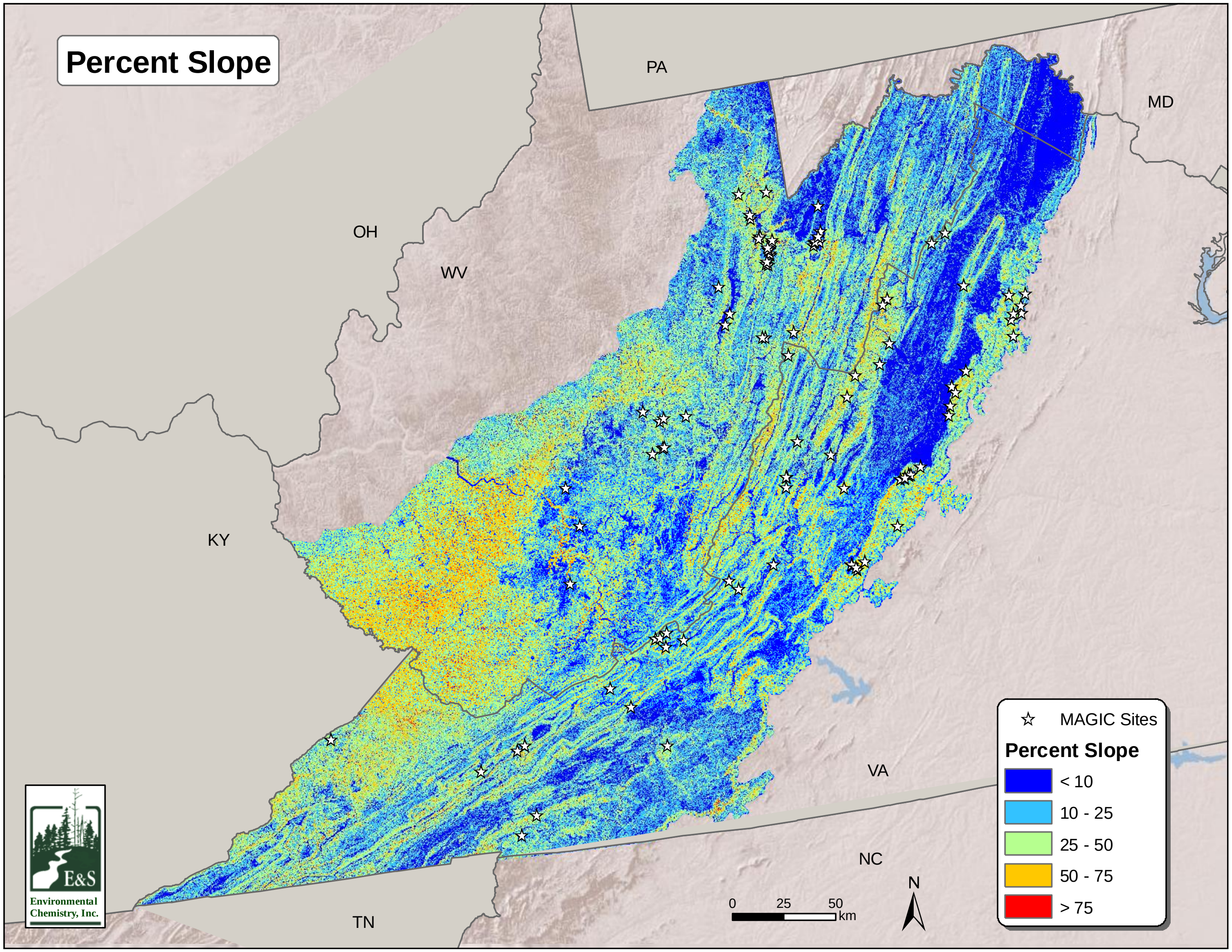


Figure 8. Spatial pattern in percent watershed slope across the study area. Also shown are MAGIC modeling sites.

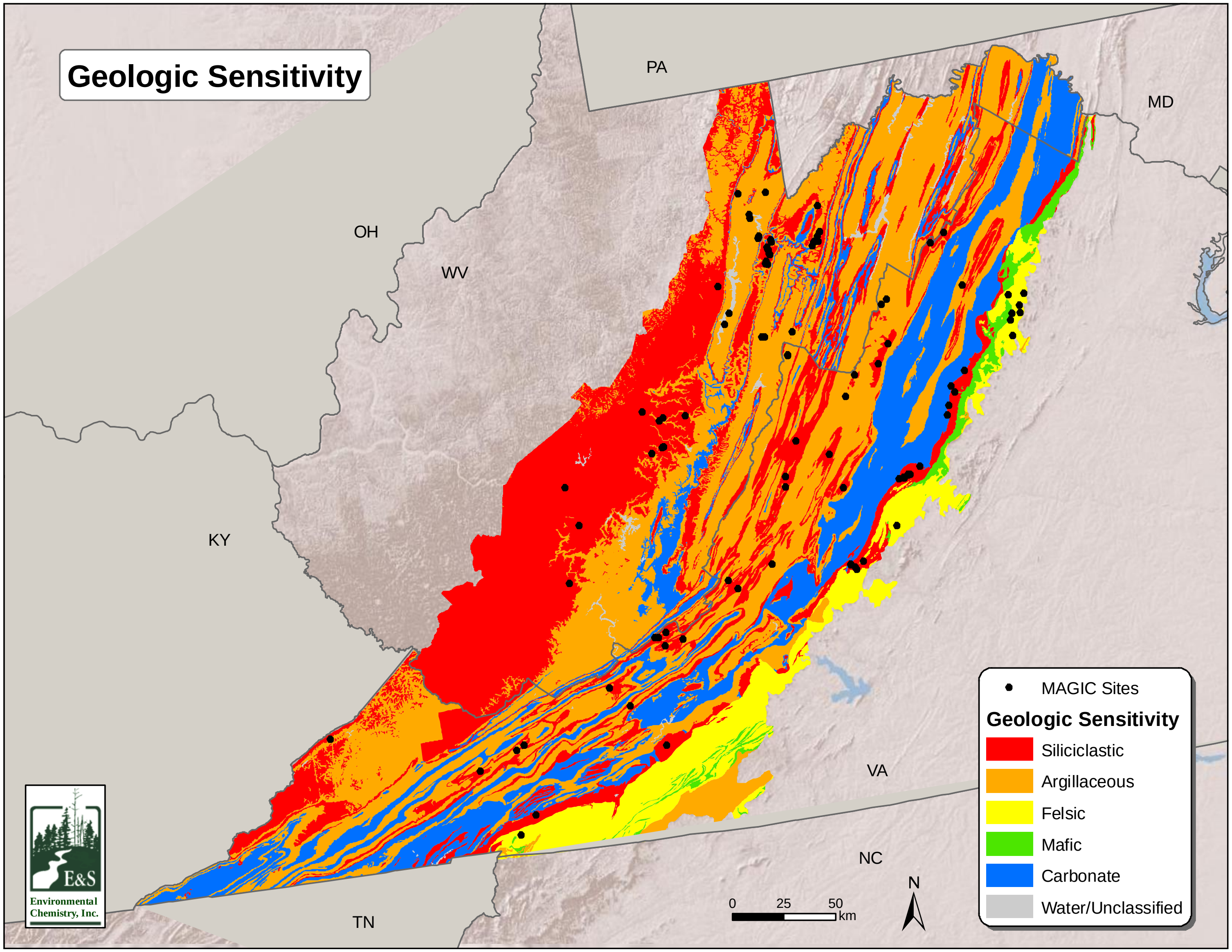


Figure 9. Geologic sensitivity classes, as determined by Sullivan et al. (2007) across the study area. Also shown are MAGIC model sampling sites.

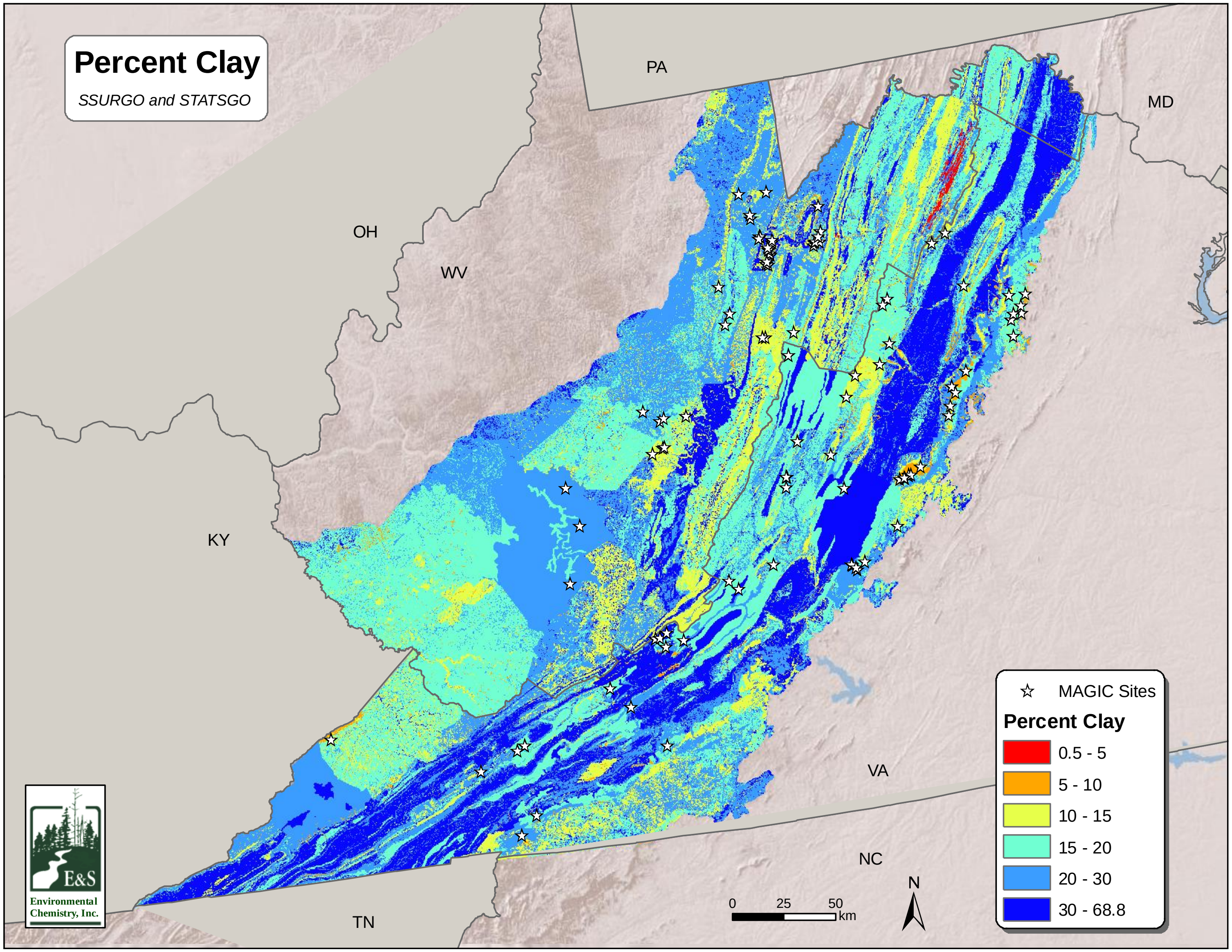


Figure 10. Percent clay in soils across the study area, based on SSURGO and STATSGO data. Also shown are MAGIC model sampling sites.

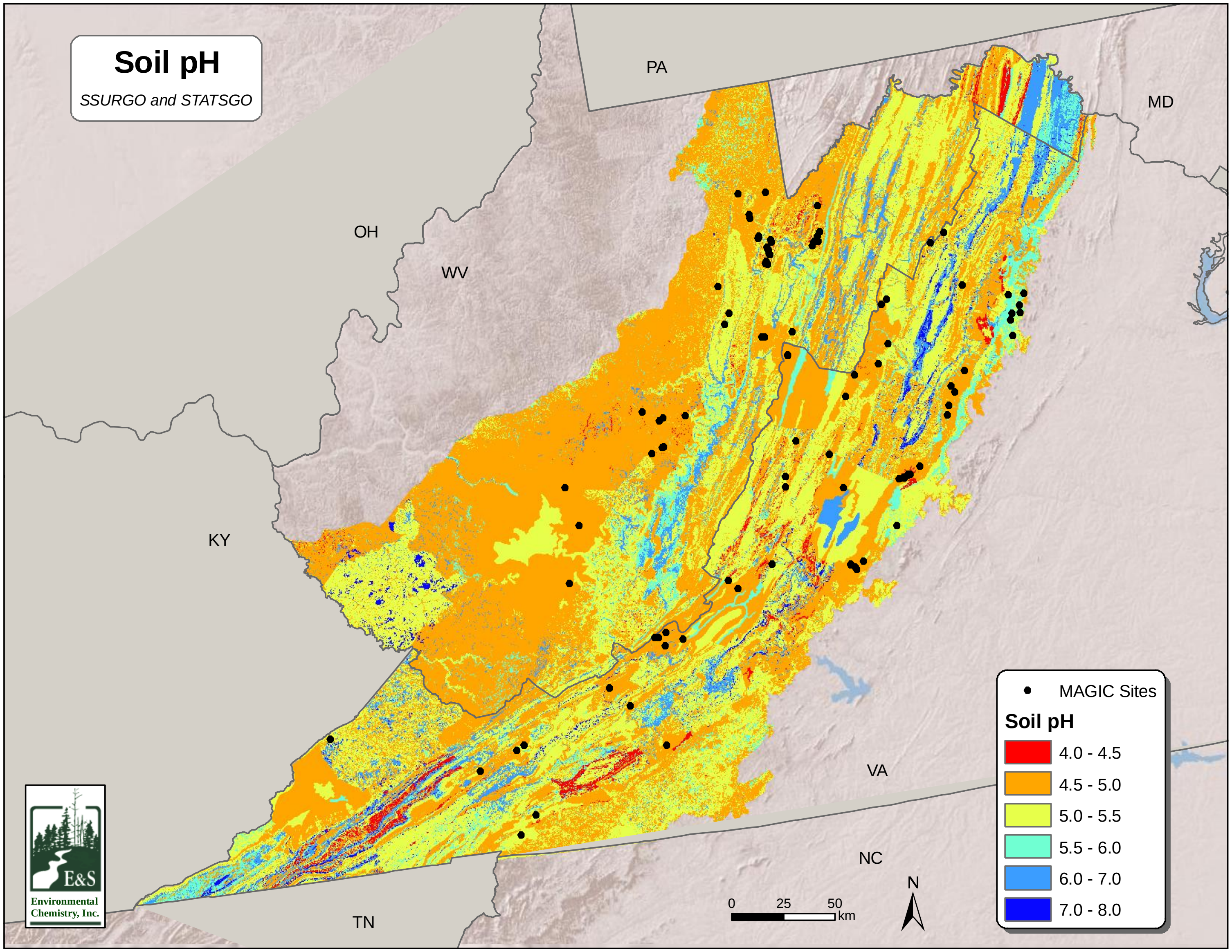


Figure 11. Soil pH across the study area, based on SSURGO and STATSGO data. Also shown are MAGIC model sampling sites.

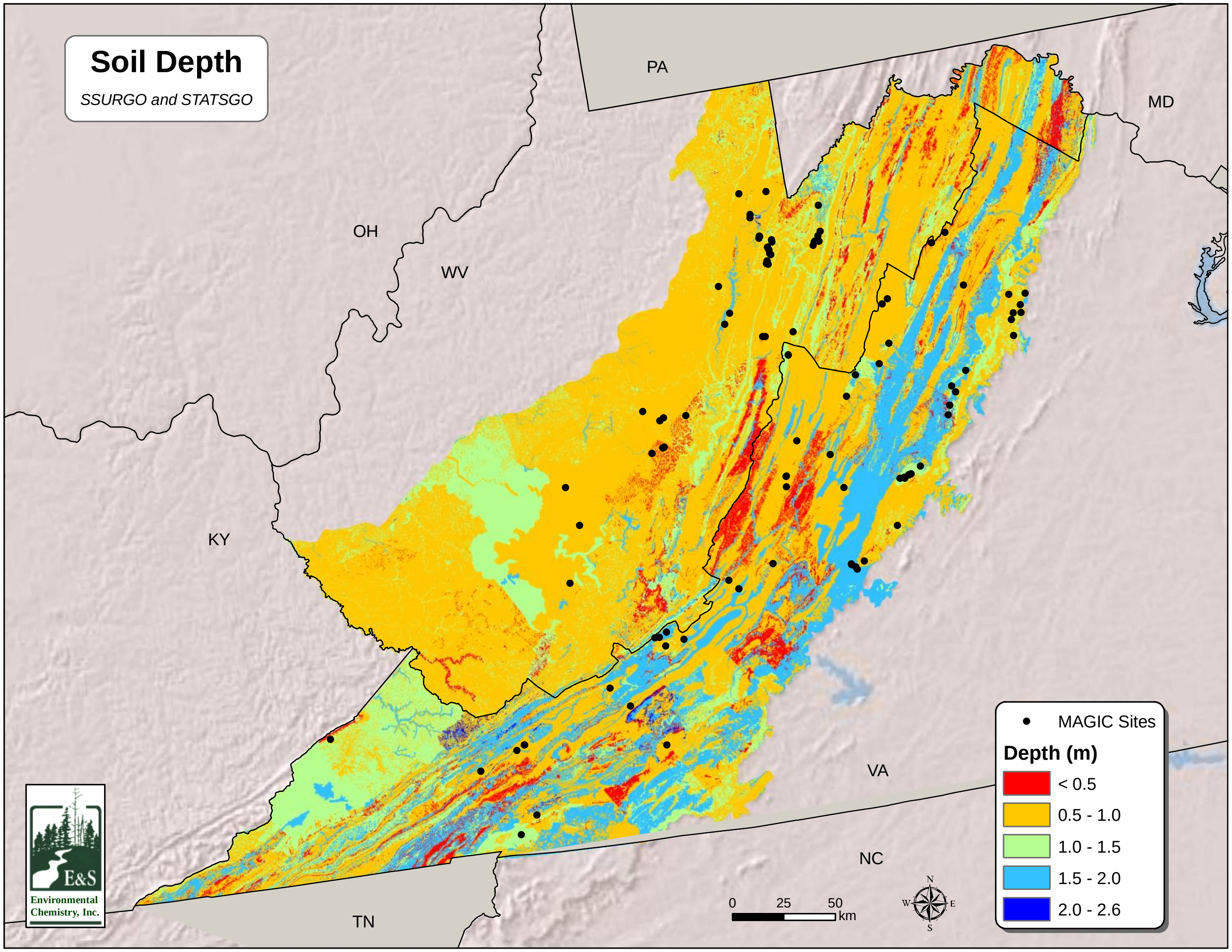


Figure 12. Soil depth to first restricting layer across the study area, based on SSURGO and STATSGO data. Also shown are MAGIC model sampling sites.

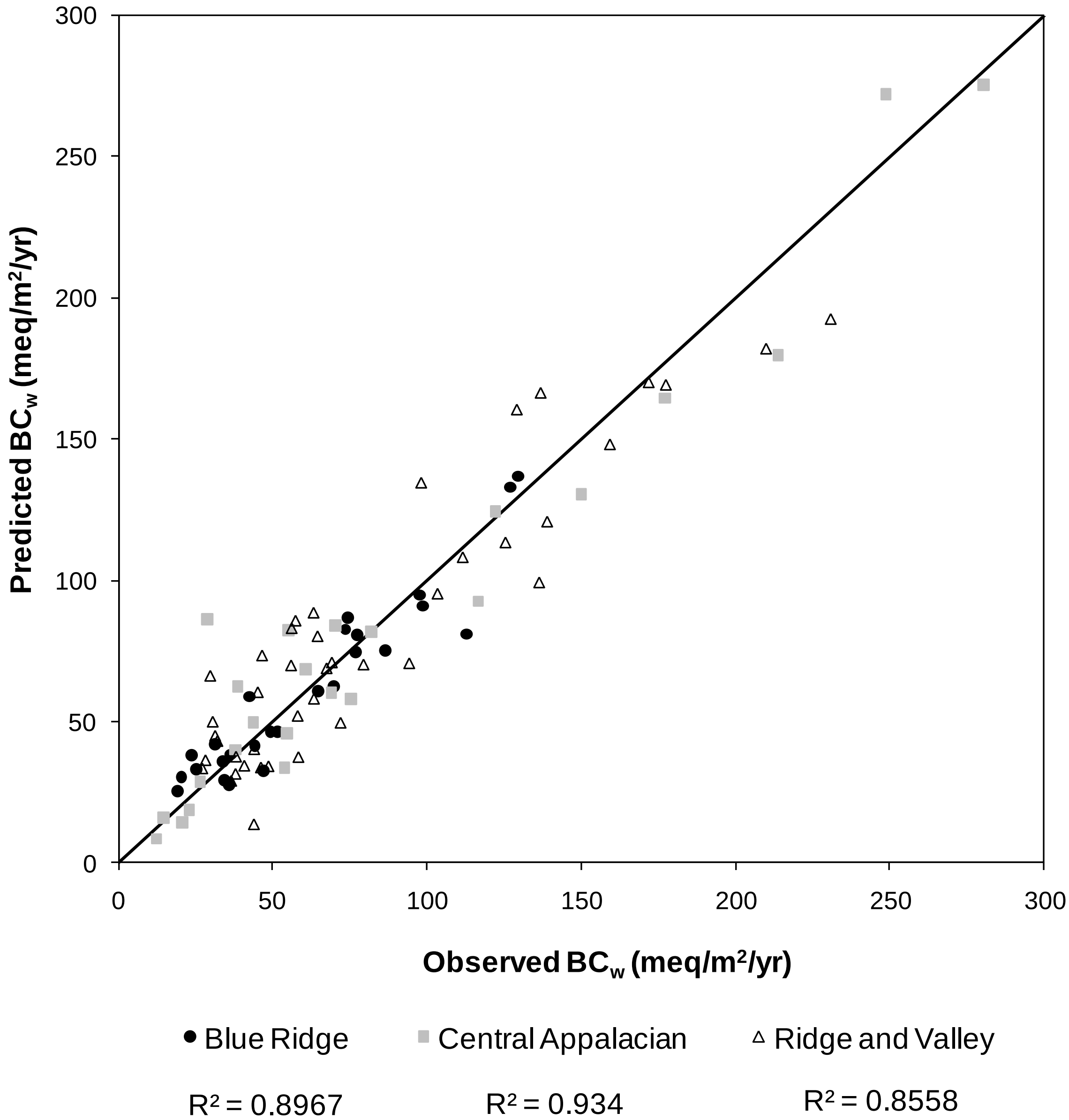


Figure 13. Predicted versus observed weathering rate, where predicted values are based on regressions using both stream chemistry and landscape variables. Observed weathering is taken from MAGIC calibrations. Sites are coded by ecoregion.

explained about two-thirds of the variation in MAGIC weathering (Figure 14), whereas the percent explained by the equations that included water chemistry were higher (85 and 93%, Table 3).

3.2 Landscape BC_w Extrapolation

The first step in extrapolating BC_w estimates to the region was to divide the study area into topographically determined watersheds. Because drainage water acidification is primarily a headwater phenomenon, these topographically determined watersheds must be small. For generating the stream network from the DEM, we specified a minimum contributing area of 0.5 km^2. In other words, the minimum drainage area that was designated as a stream watershed from the flow accumulation analysis was 0.5 km^2. The upper and lower boundaries of each down-gradient watershed was determined on the basis of tributary junctions. This process resulted in generation of a synthetic stream network that was intermediate in stream size and density between the 1:100,000 NHD stream network and the high resolution 1:24,000 NHD network (Figure 15). The typical topographically determined watersheds were on the order of 1 km^2 in area.

At each 30 x 30 m pixel, BC_w was estimated for regional CL extrapolation using the regression equations that were based on landscape variables alone. Each regression model input parameter was calculated as an upslope averaging of all cells that flowed into a given cell (except watershed area, which was calculated as the total contributing area to a given cell). A schematic example of the averaging process is given in Figure 16 for the predictor variable soil pH. The upslope average soil pH was calculated for each cell as the average of all cells that flow into that cell. This same process was repeated across the study region for the other regression input variables. An example watershed is shown in Figure 17, where soil % clay data from SSURGO (shown in Figure 17A) are averaged in an upslope fashion to yield continuous average soil % clay for each pixel in the Meadow Run watershed in Shenandoah National Park (Figure 17B). The boundary of the Meadow Run watershed is determined by the sampling location at the base of the watershed. The sampled watershed contains three topographically determined watersheds within it, each created based on the flow accumulation method, using a minimum topographically determined watershed area of 0.5 km^2 and downslope end determined on the basis of topographically determined stream junctions. Thus, the Meadow Run watershed contains three topographically determined subwatersheds, which differ in their clay content as represented

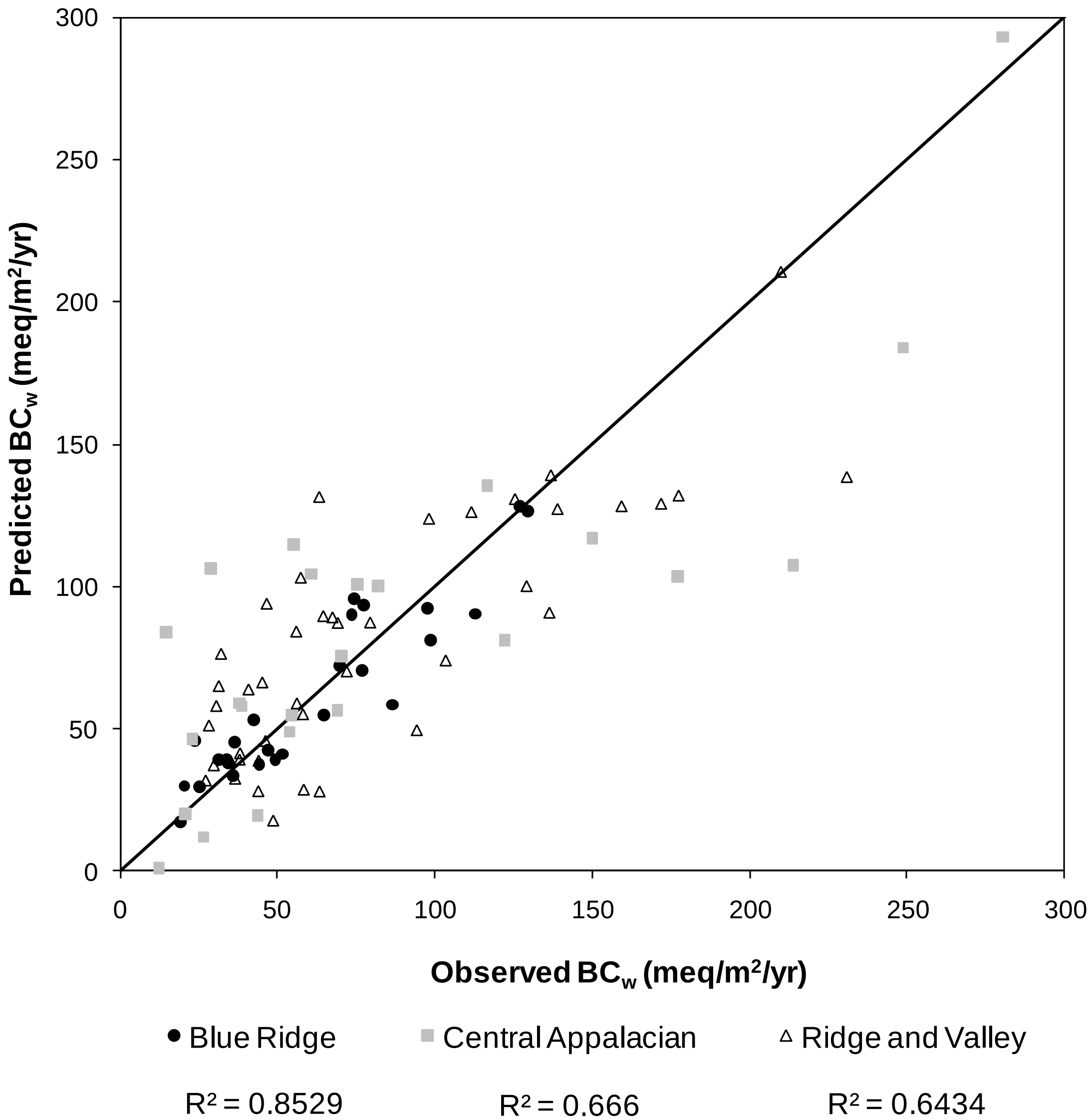


Figure 14. Predicted versus observed weathering rate, where predicted values are based on regressions using only landscape variables. Observed weathering is taken from MAGIC calibrations. Sites are coded by ecoregion.

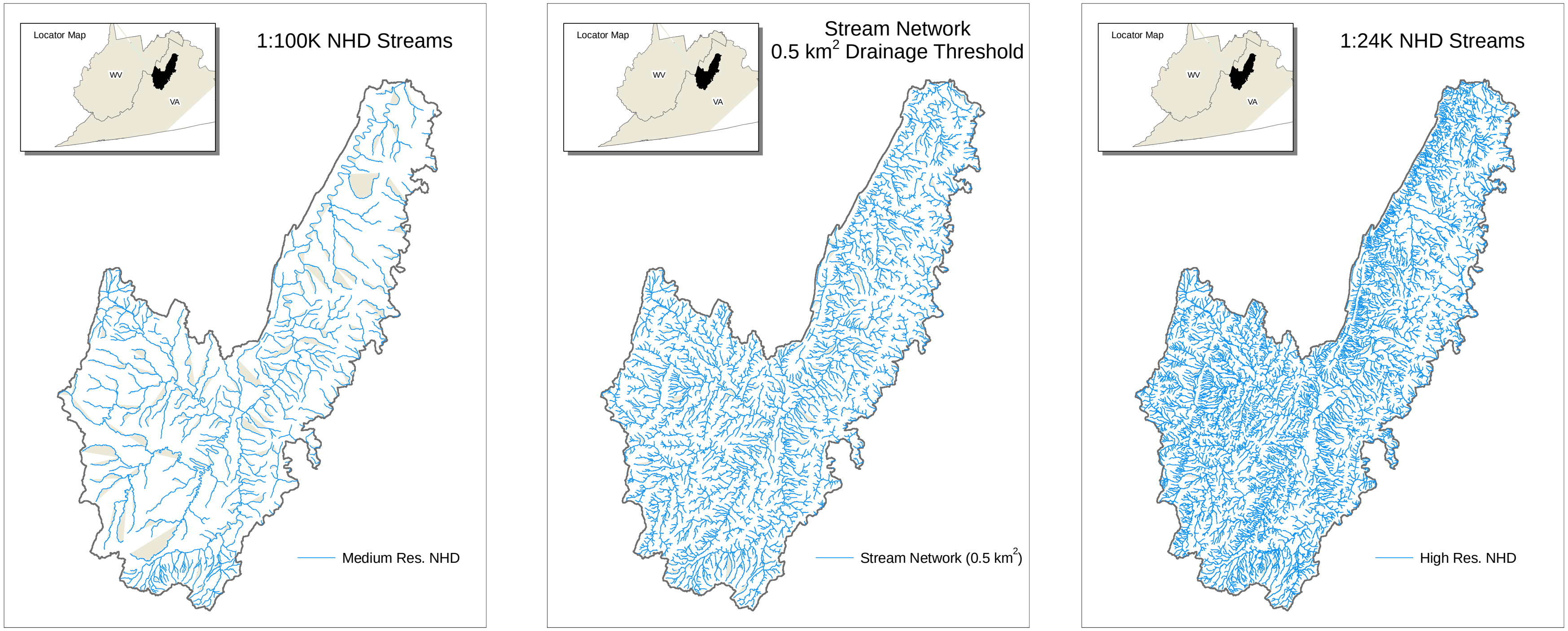


Figure 15. Stream network generated using a 0.5 km^2 contributing area minimum threshold and stream junction locations to define watersheds. This topographically determined stream network (center) has resolution that is generally between the moderate resolution (left) and high resolution (right) NHD datasets.

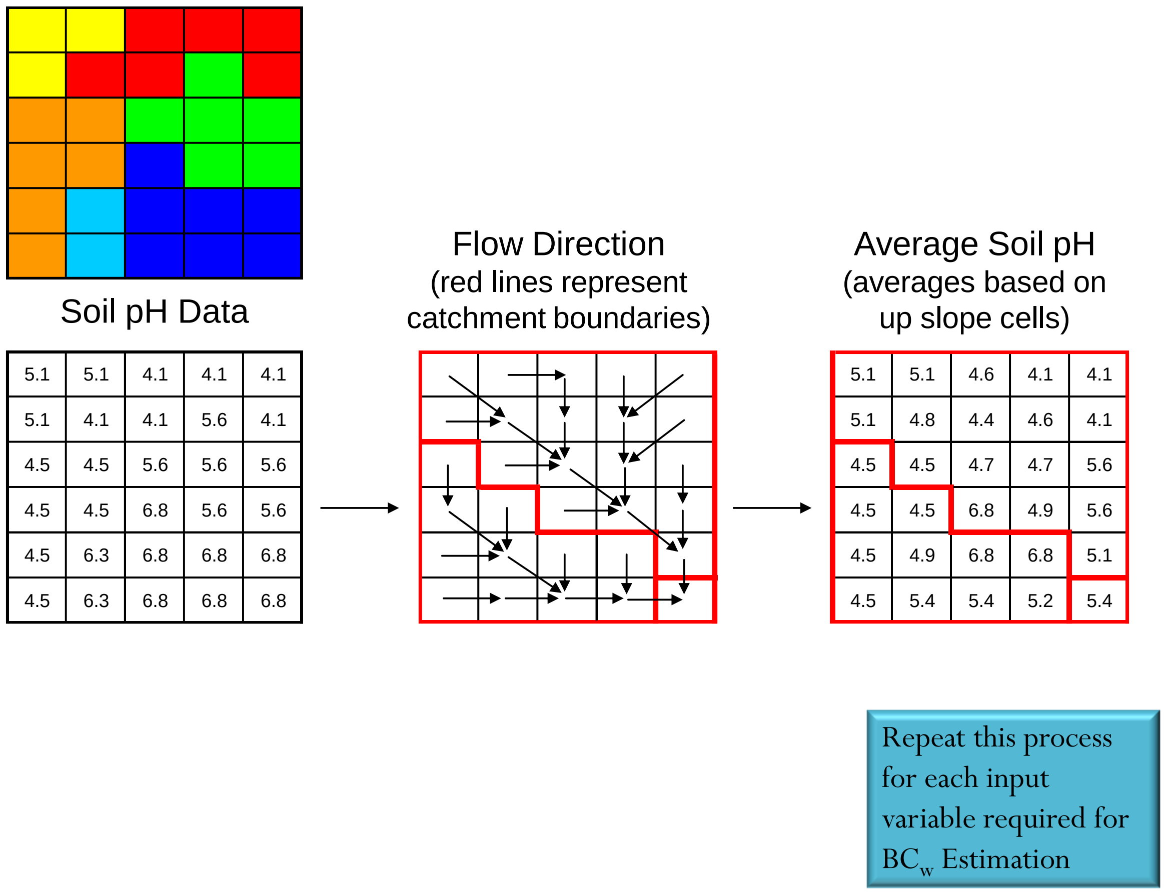


Figure 16. Example illustration of combining soil pH data (grids from SSURGO) with NHD-Plus data derived from the DEM to estimate the soil pH value in each grid cell based on an average of all upslope cells that flow into a given cell.

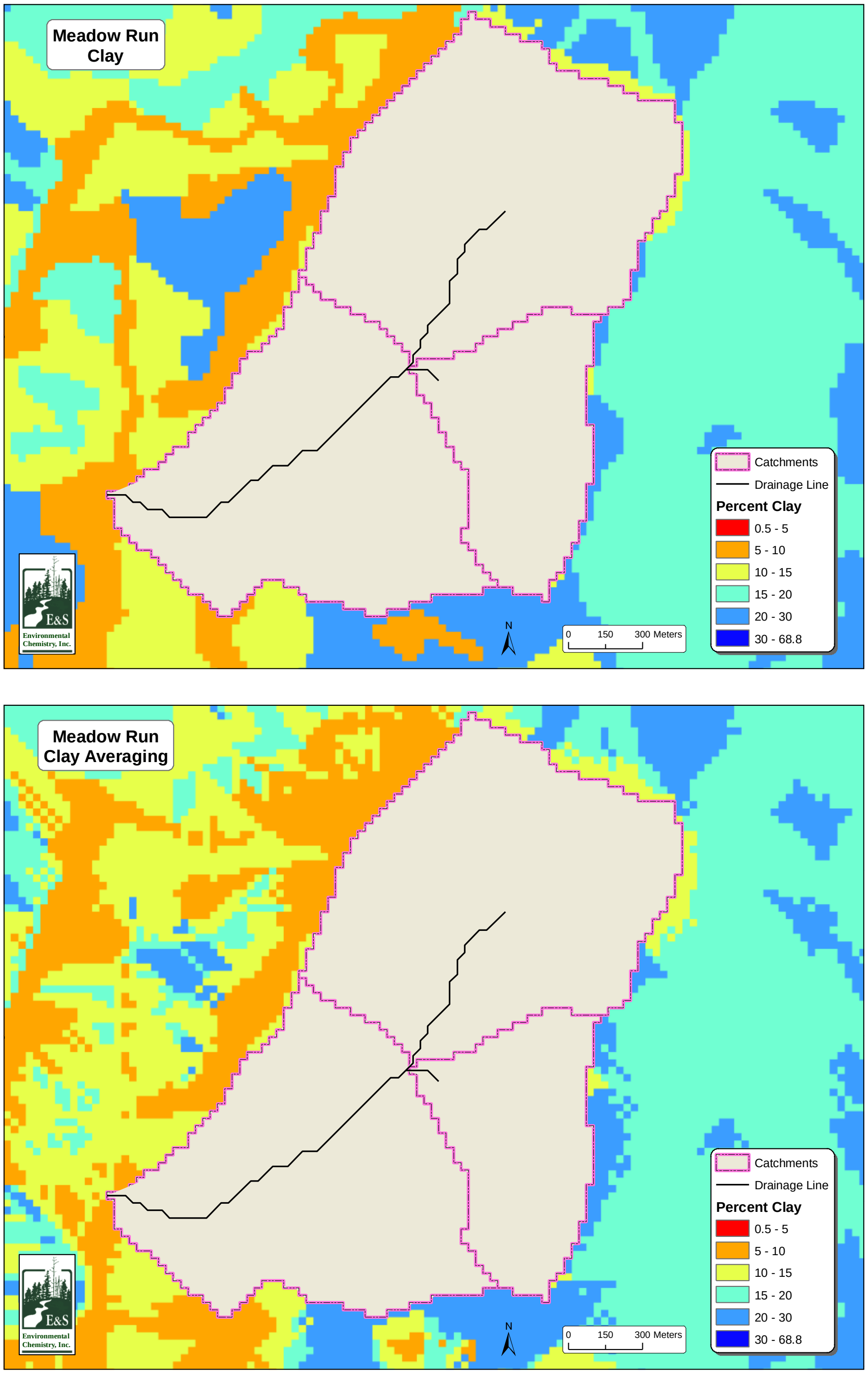


Figure 17. Example of continuous upslope averaging of clay data to derive for each 30-m grid cell an average value of all upslope cells that flow into a given cell. A) Data directly from SSURGO, B) continuous flow-averaged data. Note that grid cells towards the upper left tend to have relatively low percent clay, whereas cells towards the lower right have relatively high percent clay. Grid cells along the stream itself (Meadow Run in Shenandoah National Park) have intermediate values, reflecting the averaging of all upslope cells that contribute drainage to the stream cells.

in SSURGO. The continuous averaging process (Figure 17B) shows upslope average values in some cases tracing the flow pattern of the topographically determined stream as the % clay changes along the drainage path across the landscape.

Based on calculations for each pixel, using the ecoregion-specific regression equations given in Table 3, BC_w was calculated across the study area (Figure 18). Results of that calculation for the Meadow Run watershed are given in Figure 19. Meadow Run has the lowest ANC among the sites in Shenandoah National Park that are routinely monitored for stream chemistry (Sullivan et al. 2003). Consequently, large portions of the watershed showed low estimates of weathering (less than 50 meq/m^2/yr). Nevertheless, some portions of the Meadow Run watershed show somewhat higher weathering (between 50 and 100 meq/m^2/yr). Despite the contribution of drainage from the areas that are characterized by higher weathering, the pixels along the topographically determined stream are entirely in the lowest weathering class. This is because the BC_w in each pixel reflects an average of all upslope contributing pixels at each point along the stream, rather than just the adjacent pixels. This illustrates the value of using an upslope averaging approach to integrate features of the landscape throughout the entire drainage area that contributes runoff to a given stream location.

3.3 Calculations of Critical Load of Acidity

The CL equation (Equation 1) has four terms. The BC_w term is generally quantitatively highest and most uncertain. Results applied to the calculation of BC_w were provided in the section above. Results for BC_{dep}, Bc_{up}, and ANC_{limit} are presented below. Regional BC_{dep} is shown in Figure 20. It ranges from low values in the range of 6 to 10 meq/m^2/yr in northern Virginia to the range of 15 to 20 meq/m^2/yr in West Virginia and smaller portions of Virginia. Base cation uptake was set to zero in protected areas such as Shenandoah National Park and the various Wilderness areas, but increased to over 20 meq/m^2/yr in loblolly-shortleaf pine, oak-pine, and oak hickory forests in unprotected areas (Figure 21).

Runoff from the USGS grid, based on 1 km grid cells, was too coarse for this study (Figure 22A). Our regional estimates of runoff, calculated using PRISM model estimates of precipitation and elevation, yielded much finer resolution (Figure 22B) that more closely corresponded with terrain differences. The combination of runoff and the selected critical ANC values to protect aquatic biota yielded spatially variable ANC_{limit} values that varied several fold.

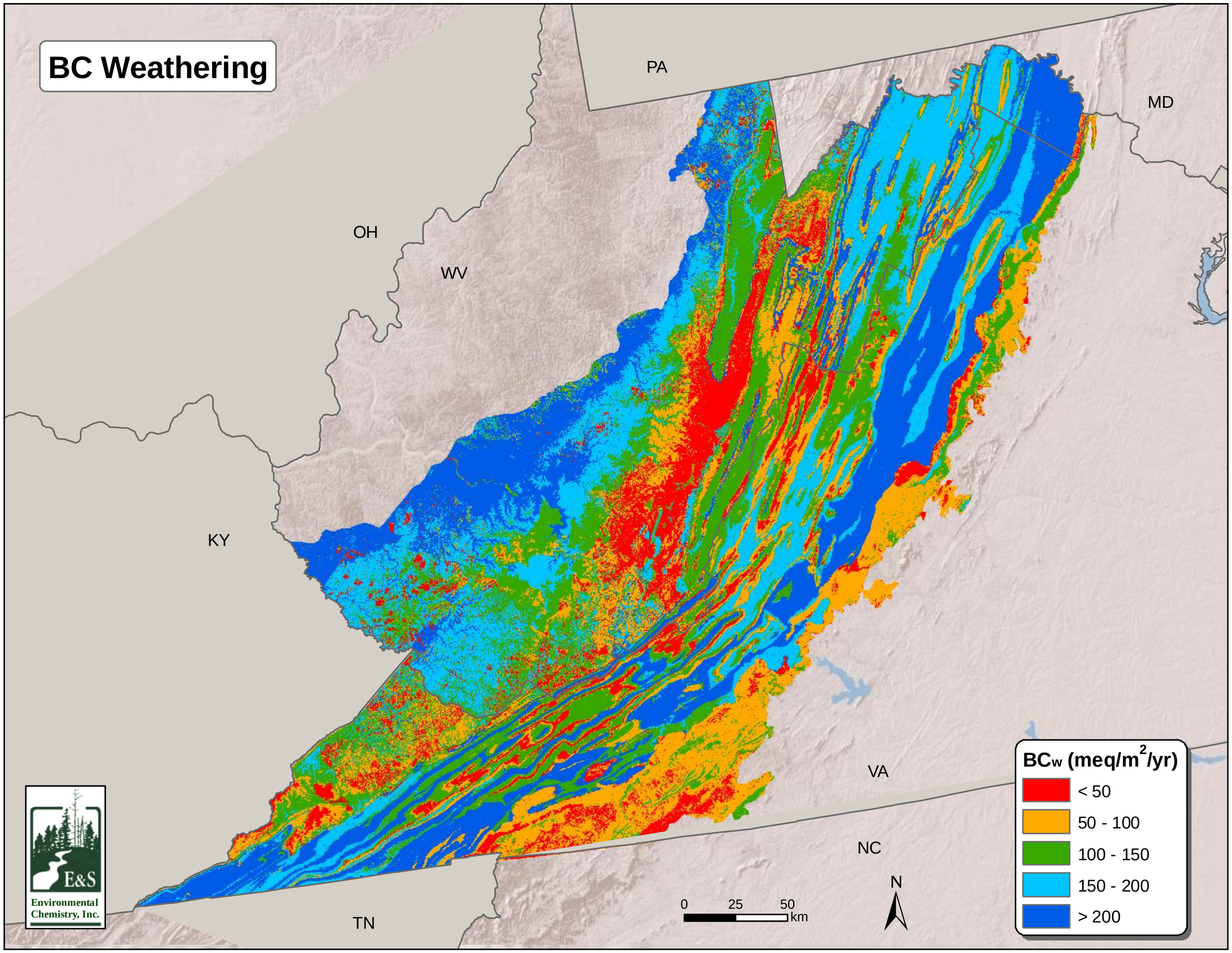


Figure 18. Calculated values of BC_w for each 30-m grid cell in the study area, based on the regression relationships that were developed using landscape variables.

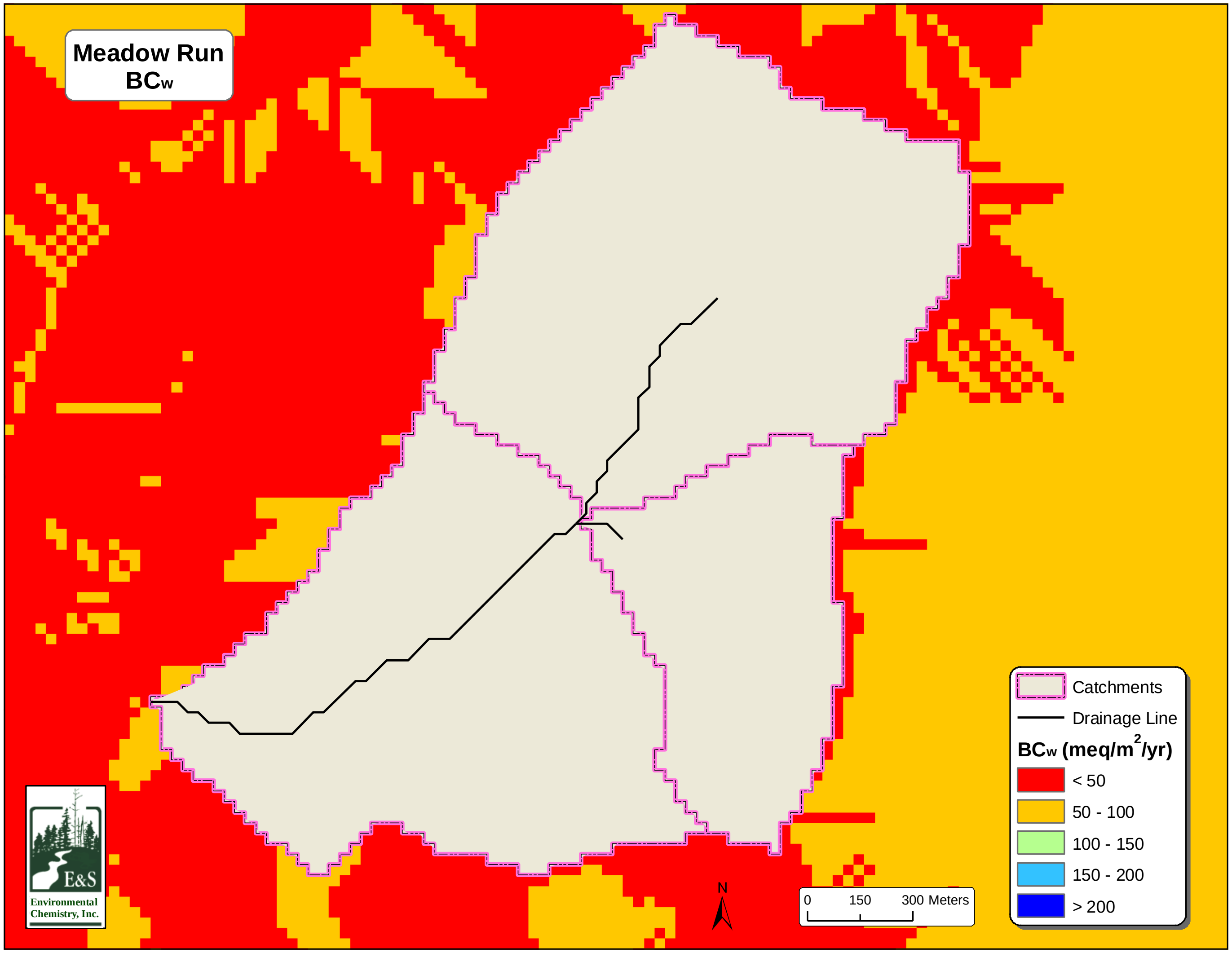


Figure 19. BC_w estimates for each 30-m pixel in the Meadow Run watershed in Shenandoah National Park, developed based on continuous downslope averaging of each variable used to calculate BC_w within the Blue Ridge ecoregion (% siliciclastic lithology, % clay in soil, and soil depth). These estimates of BC_w within each grid cell were combined with estimates for each grid cell of the other terms in the SSWC model (BC_{dep}, Bc_{up}, and ANC_{limit}) to calculate CL.

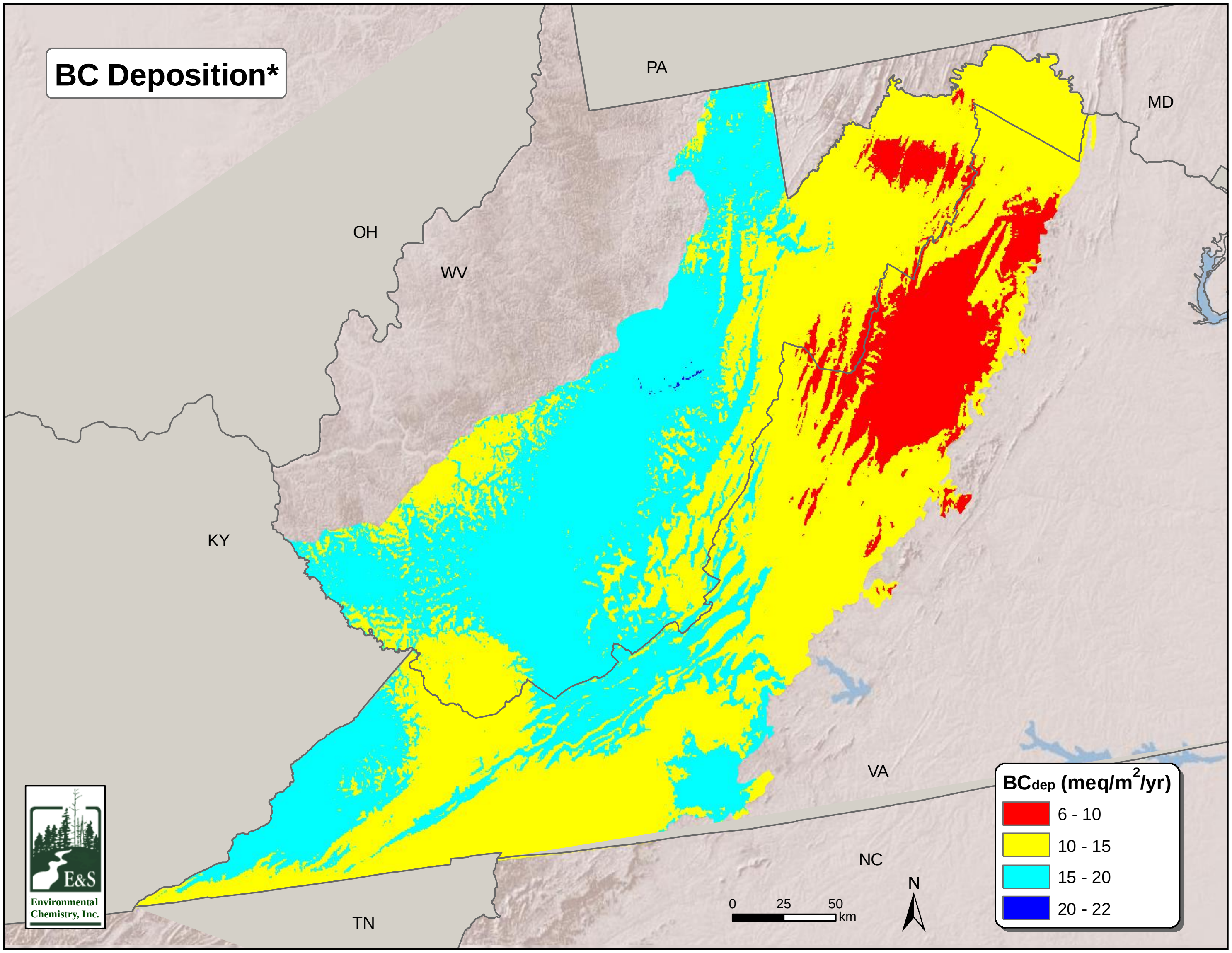


Figure 20. Base cation deposition (BC_{dep}) across the study region, Cl^- corrected, calculated as the sum of wet deposition (five-year average centered on 2002 of interpolated NADP wet deposition measurements using the Grimm and Lynch [1997] approach) and dry deposition (literature values of dry as percentage of wet; Baker et al. 1991).

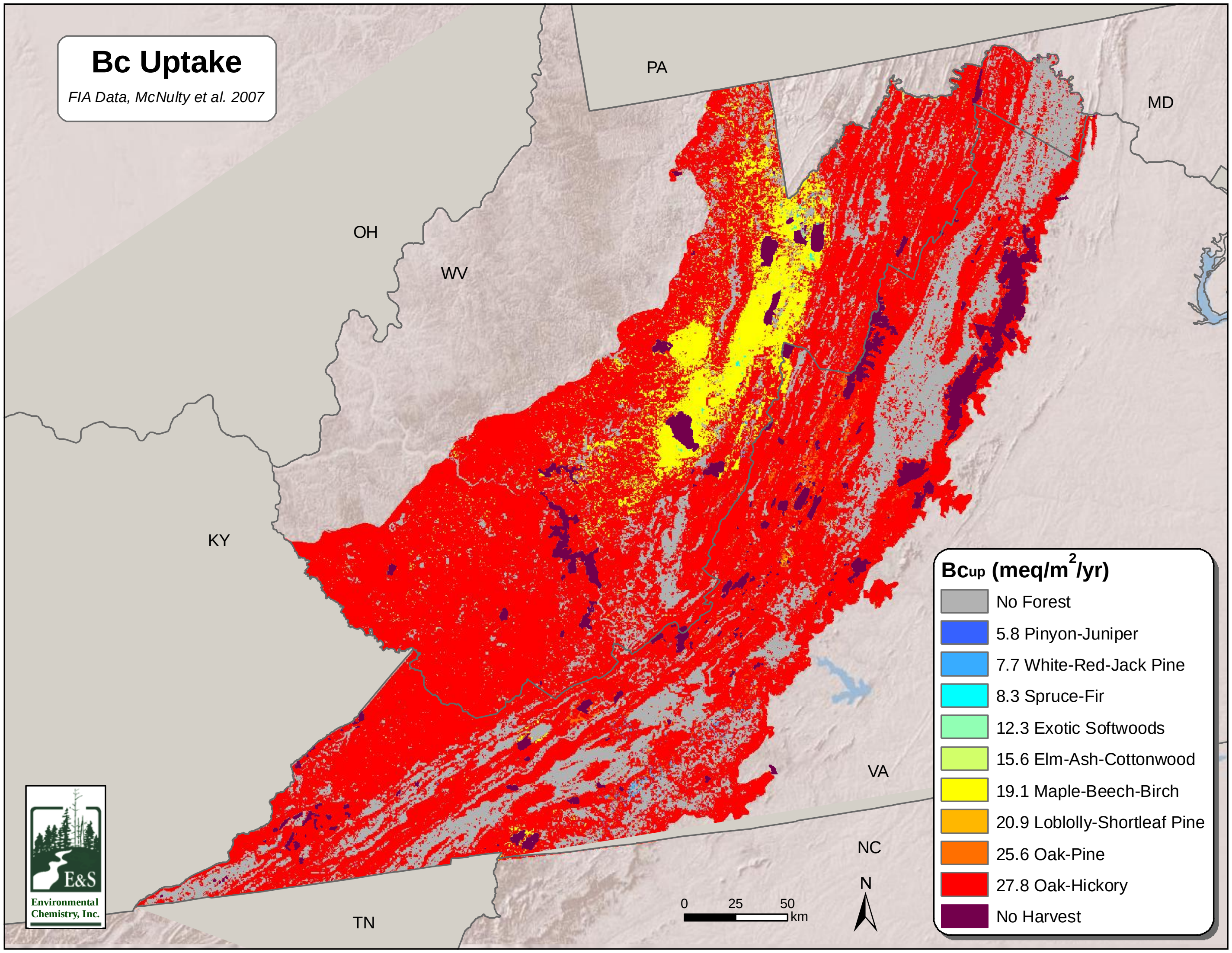
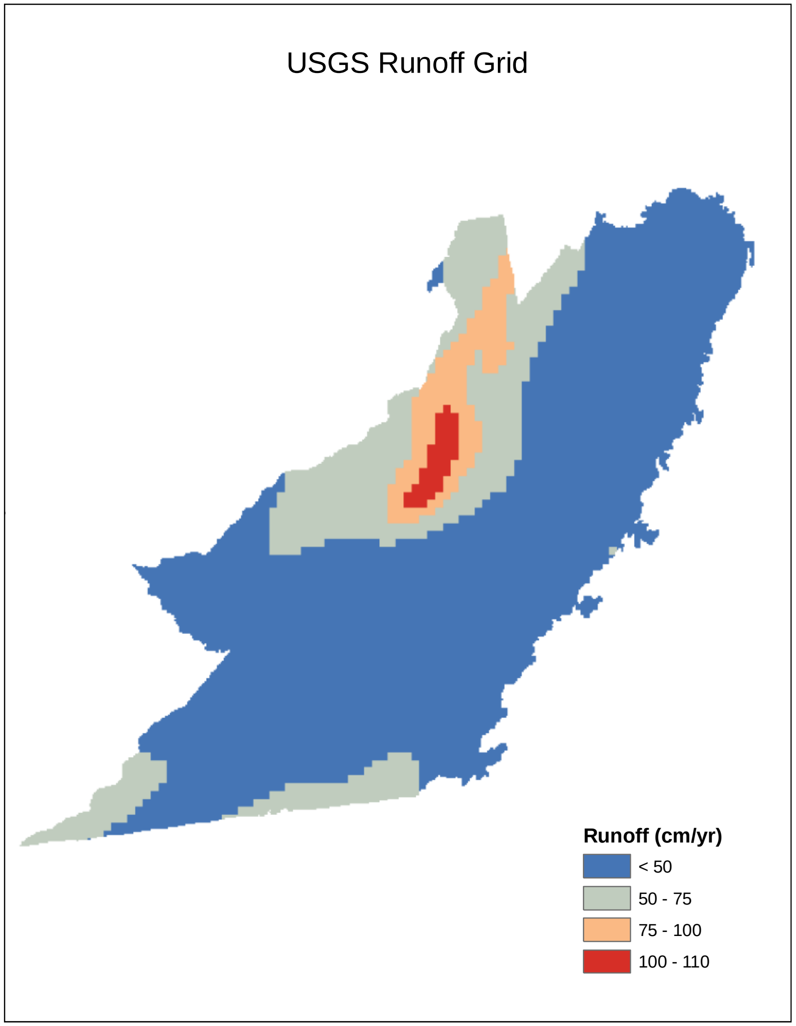


Figure 21. Base cation uptake (Bc_{up}) across the study region, based on uptake estimates for nine Forest Inventory Analyses (FIA) forest types (McNulty et al. 2007) assuming an annual harvest rate of 65% of the annual volume increment. Harvest is assumed to be zero in protected areas such as national parks, Wilderness areas, and other preserves.



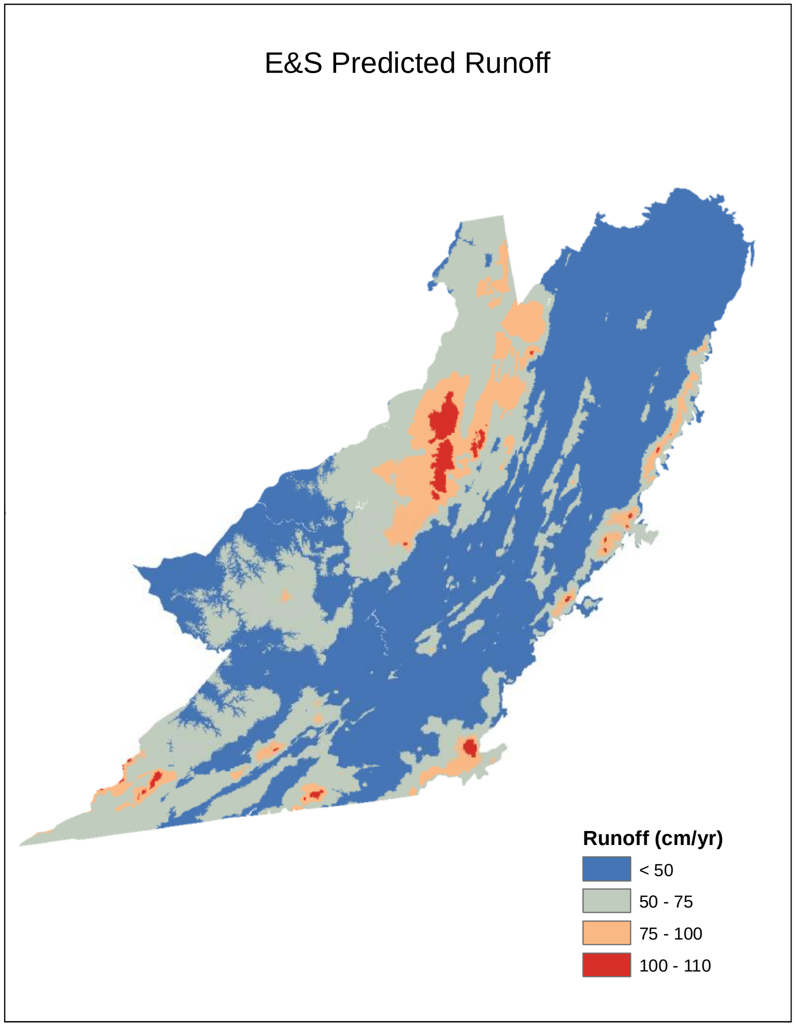


Figure 22. Runoff estimates across the study areas. A) USGS coarse runoff grid, B) E&S estimated runoff, based on measured discharge within the study area and a regression equation to predict runoff from precipitation (PRISM model) and elevation (r^2=0.91). The upper and lower bounds of the predicted runoff distribution were truncated so as not to extend beyond the range of values determined buy USGS. Note the finer resolution of the E&S approach.

An example of the resulting calculation using the ANC value 20 μeq/L is shown in Figure 23. Patterns for other ANC threshold values were the same as is shown in Figure 23 for the threshold of 20 μeq/L.

Mapped results of CL calculations are provided in the body of this report for ANC threshold values of 20, 50, and 100 μeq/L. Mapped results for the threshold of 0 μeq/L ANC, which are not considered to be protective of the environment, are given in Appendix E. It should be noted that 100 μeq/L may not be an appropriate threshold for evaluation of CL in this study area. Of the 92 MAGIC modeling sites, 55 had model hindcast estimates of pre-industrial (1860) ANC below 100 μeq/L (Appendix D). Thus, it would not be reasonable to expect to recover ANC in a given stream to a value that is higher than the pre-industrial value. In contrast, only 11 of the 92 MAGIC modeled streams had estimated pre-industrial ANC below 50 μeq/L and all except 2 of those had estimated pre-industrial ANC between 40 and 50 μeq/L.

Values of each of the CL equation input terms for each of the 522 watersheds having stream chemistry are given in Appendix F. The three different methods of calculating BC_w (Table 4), when combined with all other terms in Equation 2, yield somewhat different estimates of CL for the sites for which CL was calculated using more than one approach. These site-specific CL results are given in Table F-4 of Appendix F.

Table 4. Outline of different approaches for estimating BC_w.

Approach	n	Description
Primary site-specific	92	Weathering extracted from MAGIC calibrations at sites modeled using MAGIC
Secondary site-specific	522	Weathering estimated using an ecoregion-specific regression model based on predictor variables that included site-specific stream chemistry and landscape features
Mapped regional	Entire study area	Weathering estimated using an ecoregion-specific regression model based on predictor variables that included landscape features only.

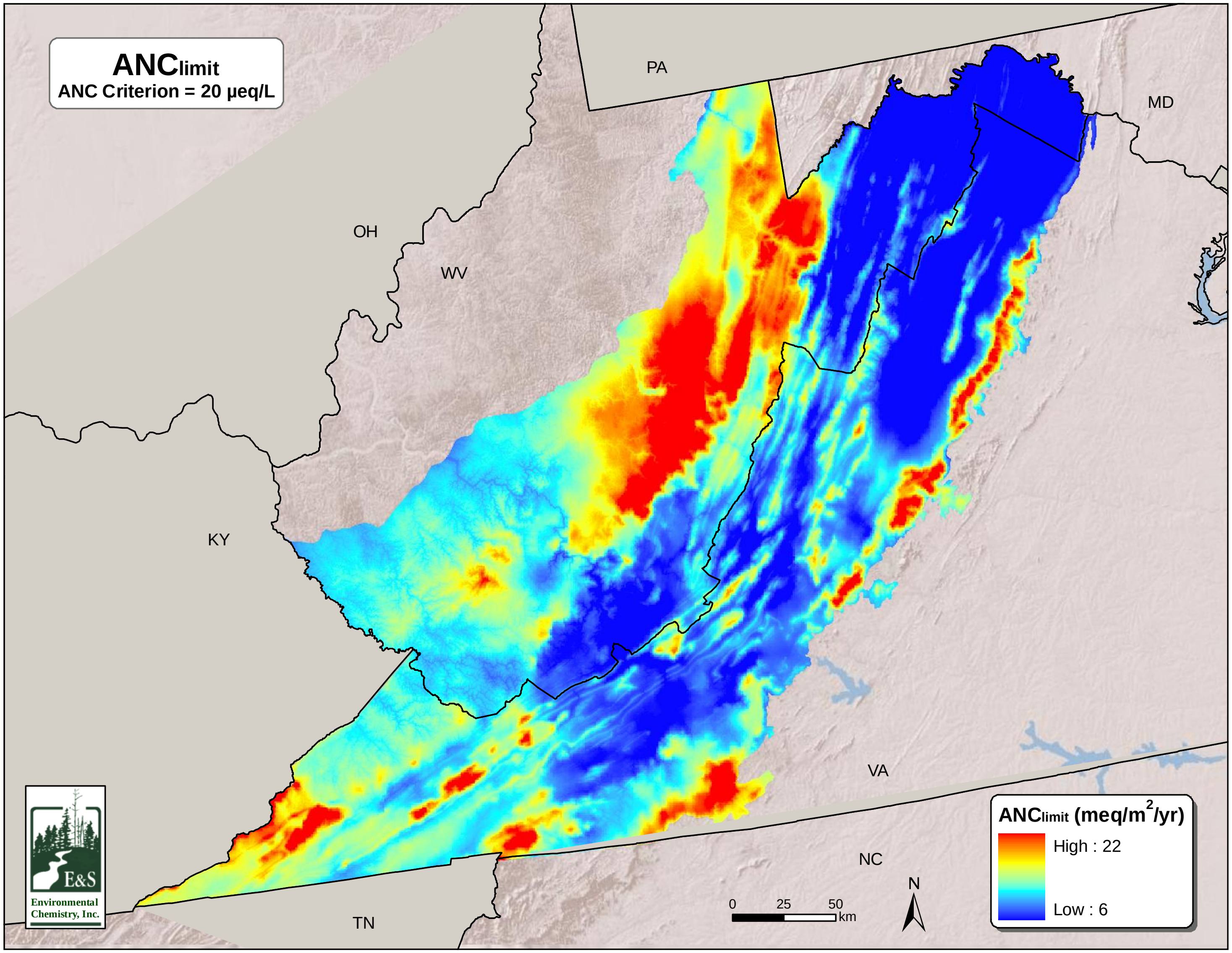


Figure 23. Distribution of calculated ANC_{limit} for the critical ANC level equal to 20 µeq/L, calculated as the product of annual runoff and the assumed critical ANC level.

3.4 Transfer of the CL Estimate from Watershed to Stream

The previous section presented our regional depiction of CL, calculated and mapped as values for small watersheds. Also of interest is a presentation of CL results for the network of streams that flow through these watersheds. Streams considered thus far in this analysis have been topographically determined streams, generated from the DEM and flow trajectory analysis. These topographically determined streams are expected to correspond approximately, but not exactly, with streams represented in the national stream network as depicted in the high-resolution NHD. It was therefore desirable to transfer our CL calculations from topographically determined watersheds to NHD streams. That step is described here.

Meadow Run is again illustrated as an example of the model input terms in Figure 24, and the resulting CL that is calculated from these terms is given in Figure 25. The representative watershed CL value is determined from the CL values calculated at each stream pixel within the watershed because the focus of this effort is on aquatic CLs. A regional watershed CL map was prepared for each critical ANC indicator value (Figures 26 through 28).

Calculated CL values for the Meadow Run watershed, as an example, were clipped to include only those pixels that lie along the topographically determined stream (Figure 29), coded for this figure to reveal the spatial variation in CL. All stream pixel values exhibited BC_w estimates that were below 50 meq/m^2/yr but, nevertheless, did reveal some spatial variation. Results of the CL calculation for these stream pixels were averaged to reflect the CL of the stream reach that flows through that watershed based on the national stream network as represented in the high-resolution NHD database. This process was completed for all watersheds and NHD stream reaches to yield a regional stream coverage that is coded by CL according to the value given to its associated watershed. An example for the southern portion of Shenandoah National Park is shown in Figure 30.

3.5 Differences Among Extrapolation Approaches

Calculated CL for the 522 stream watersheds having water chemistry data (secondary site-specific results) are shown in Figure 31. Despite the seemingly large number of sites included in the analysis, the spatial coverage is sparse. The modeled watersheds tend to be relatively small, reflecting known spatial patterns in acid sensitivity. Where larger watersheds are represented by the available stream chemistry data, their calculated CL tends to be at least moderately high (greater than 100 meq/m^2/yr).

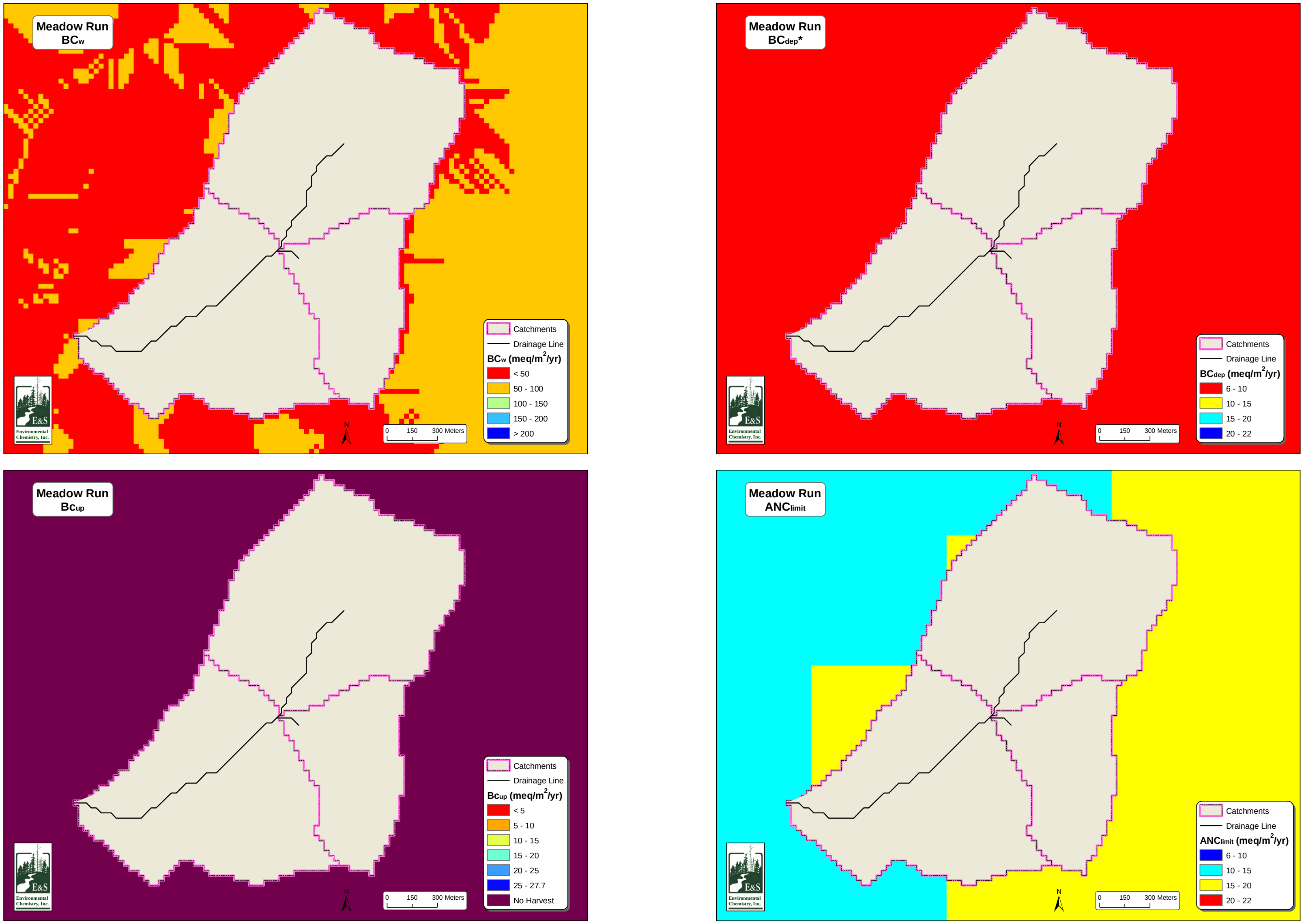


Figure 24. Example for the Meadow Run watershed in Shenandoah National Park showing the spatial coverages of each of the four terms used in the SSWC model to calculate the CL. Based on these coverages, CL was calculated for each 30-m pixel.

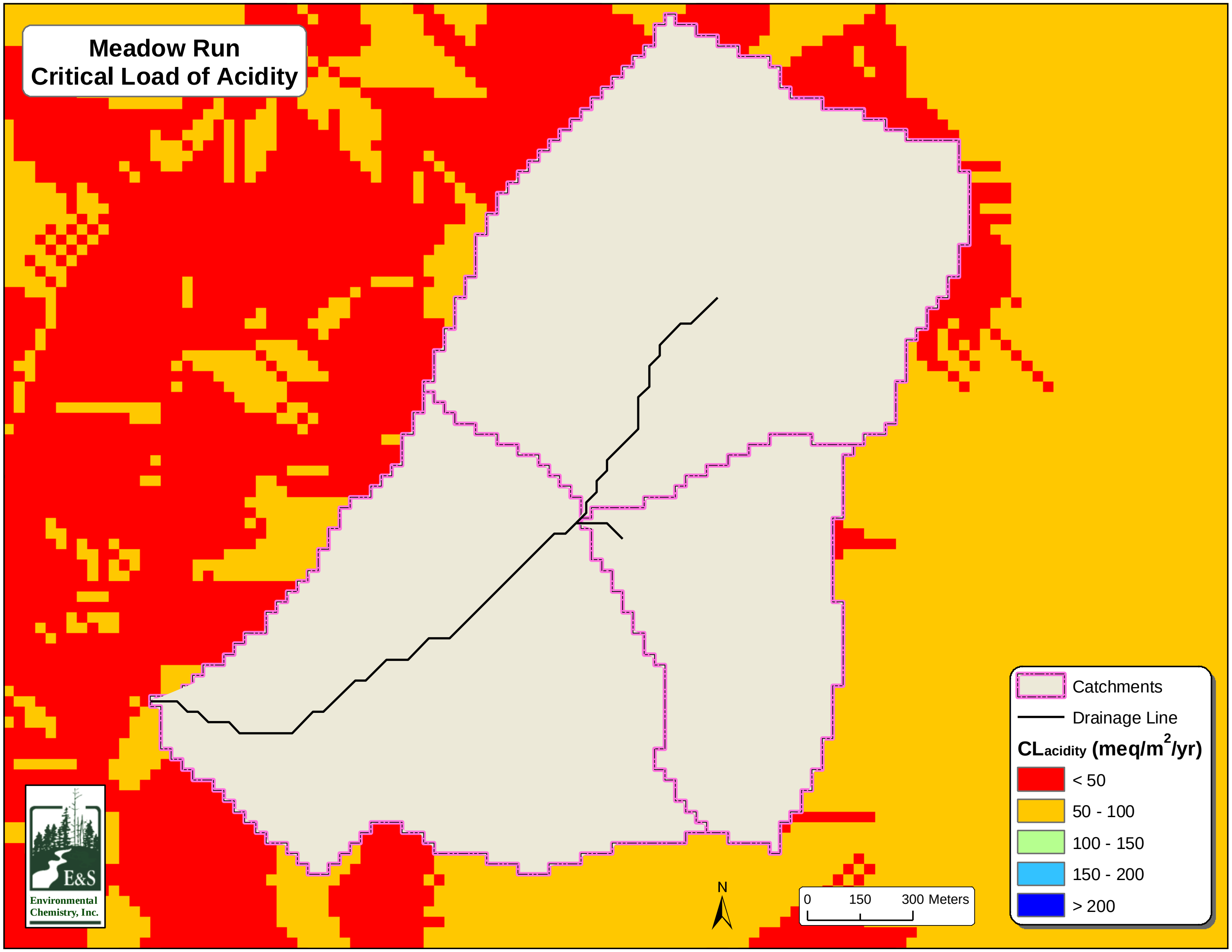


Figure 25. Calculated CL of acidity for the Meadow Run watershed in Shenandoah National Park to protect against ANC below 20 μeq/L.

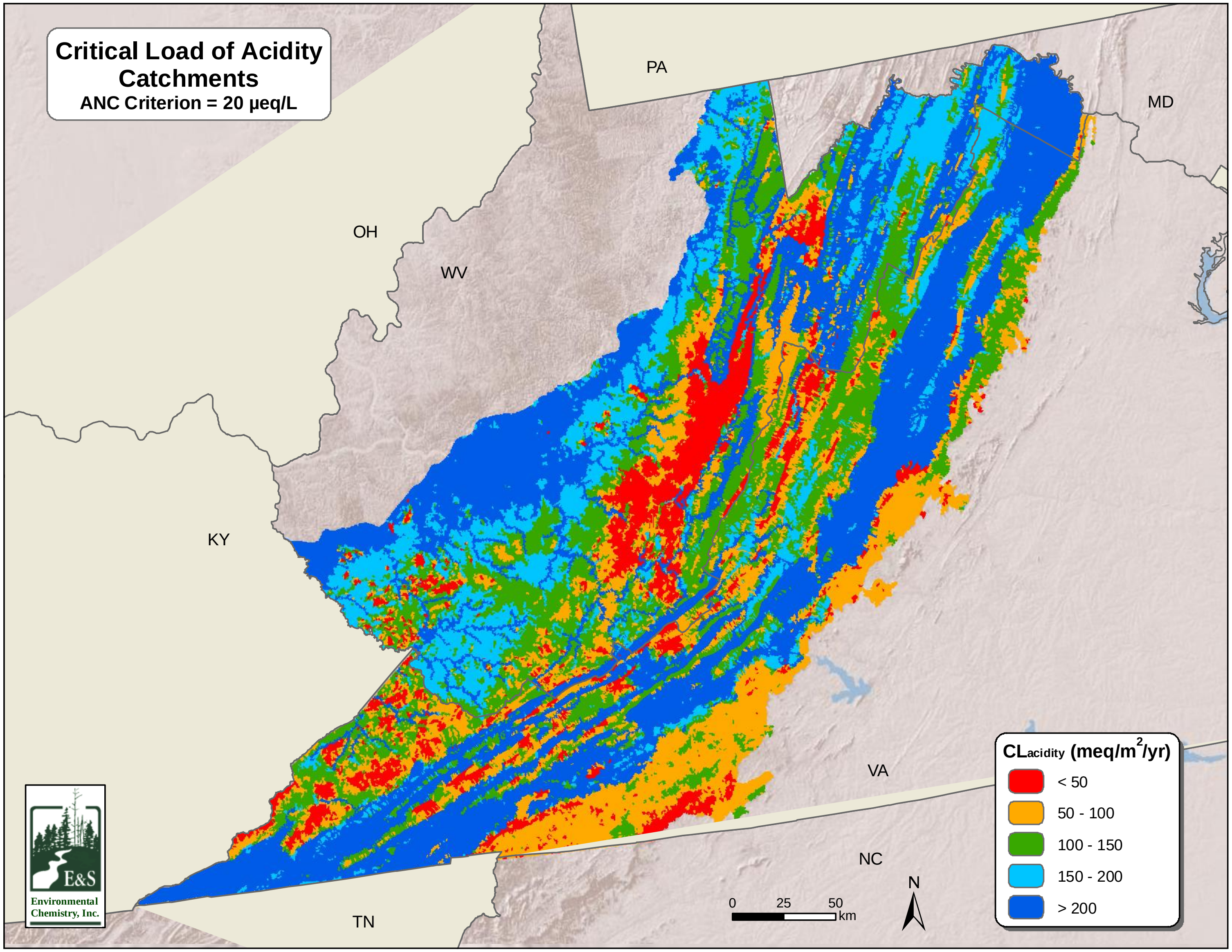


Figure 26. Final map of CL of acidity to protect stream ANC from falling below 20 µeq/L.

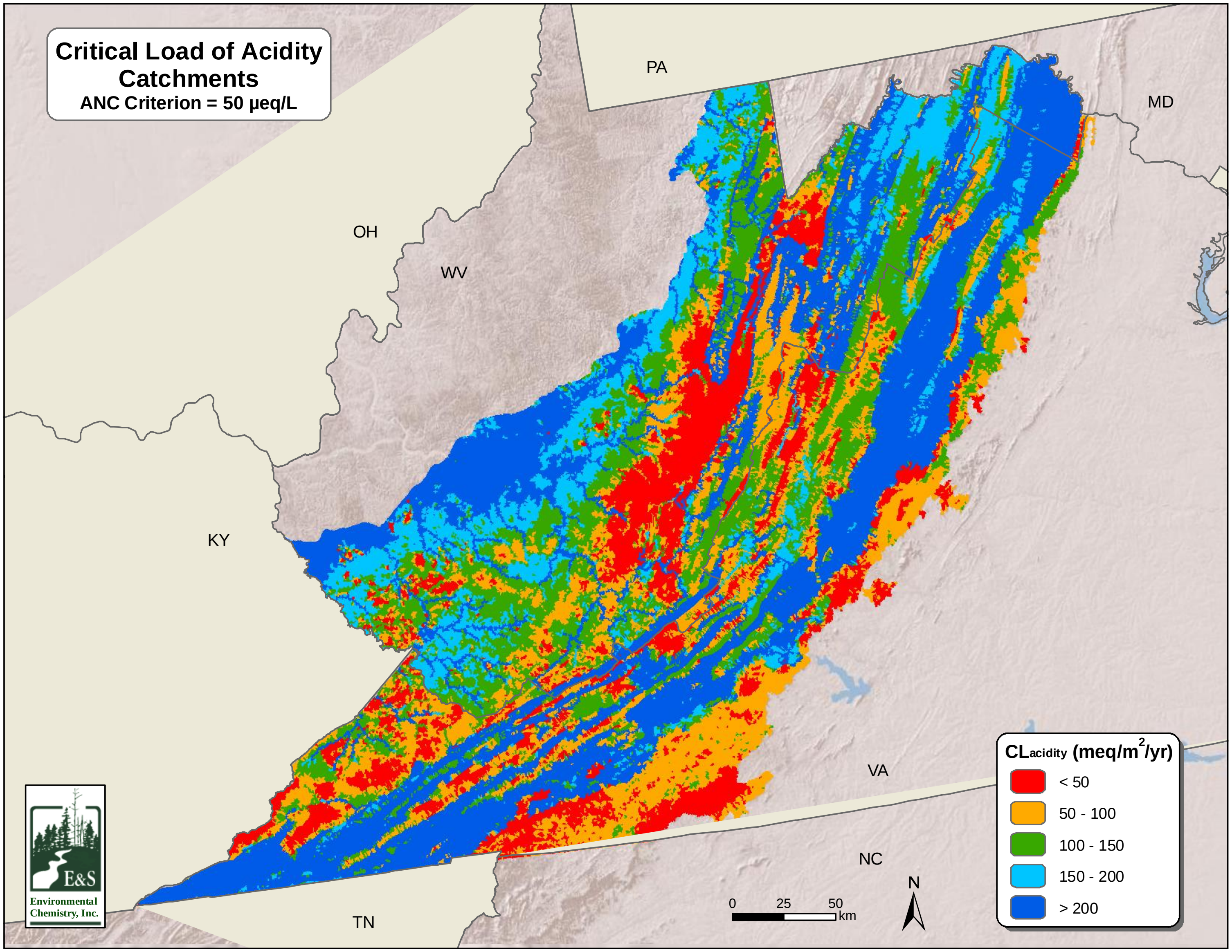


Figure 27. Final map of CL of acidity to protect stream ANC from falling below 50 µeq/L.

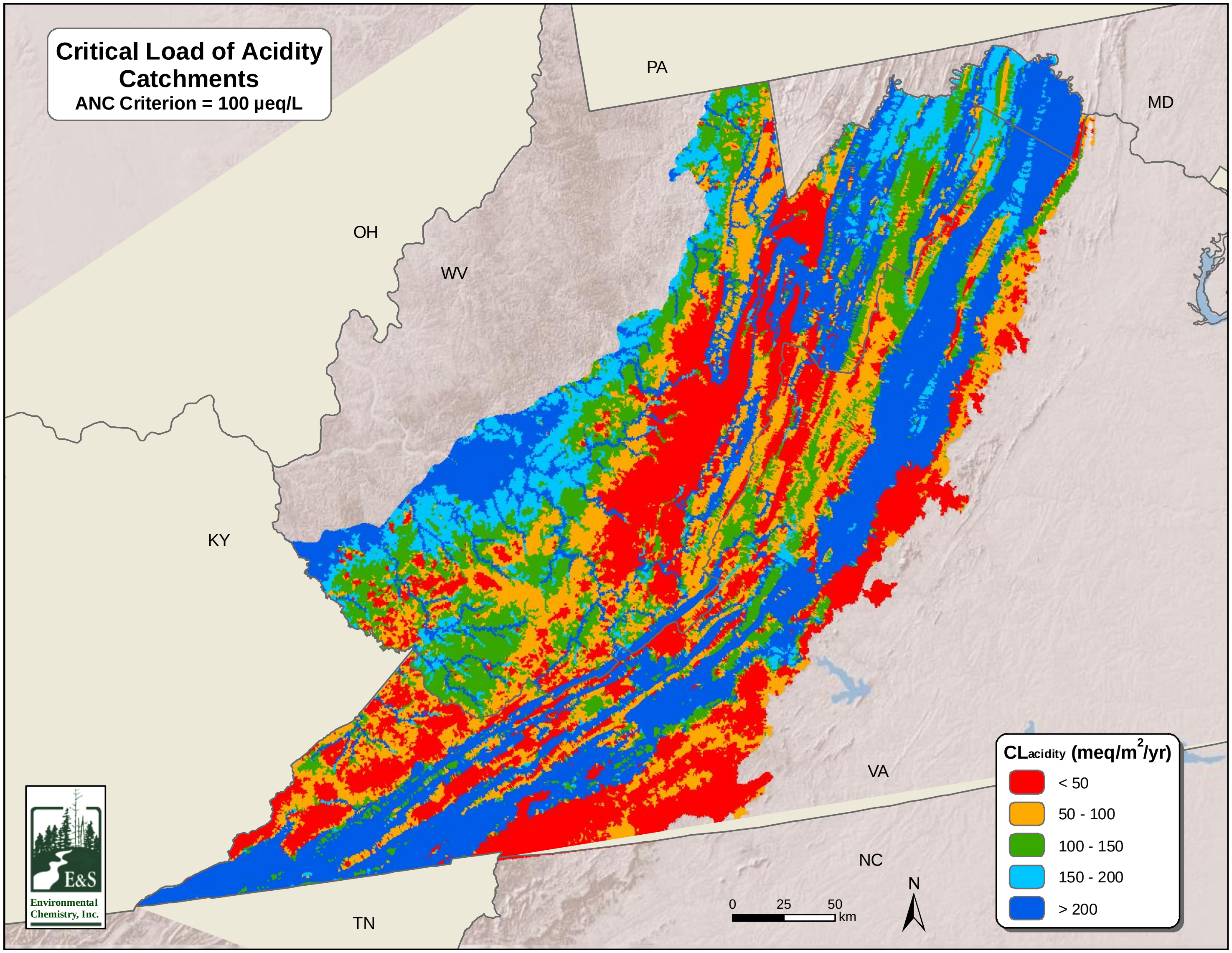


Figure 28. Final map of CL of acidity to protect stream ANC from falling below 100 µeq/L, based on an average of CL values calculated for each of the 30 m stream cells within each watershed.

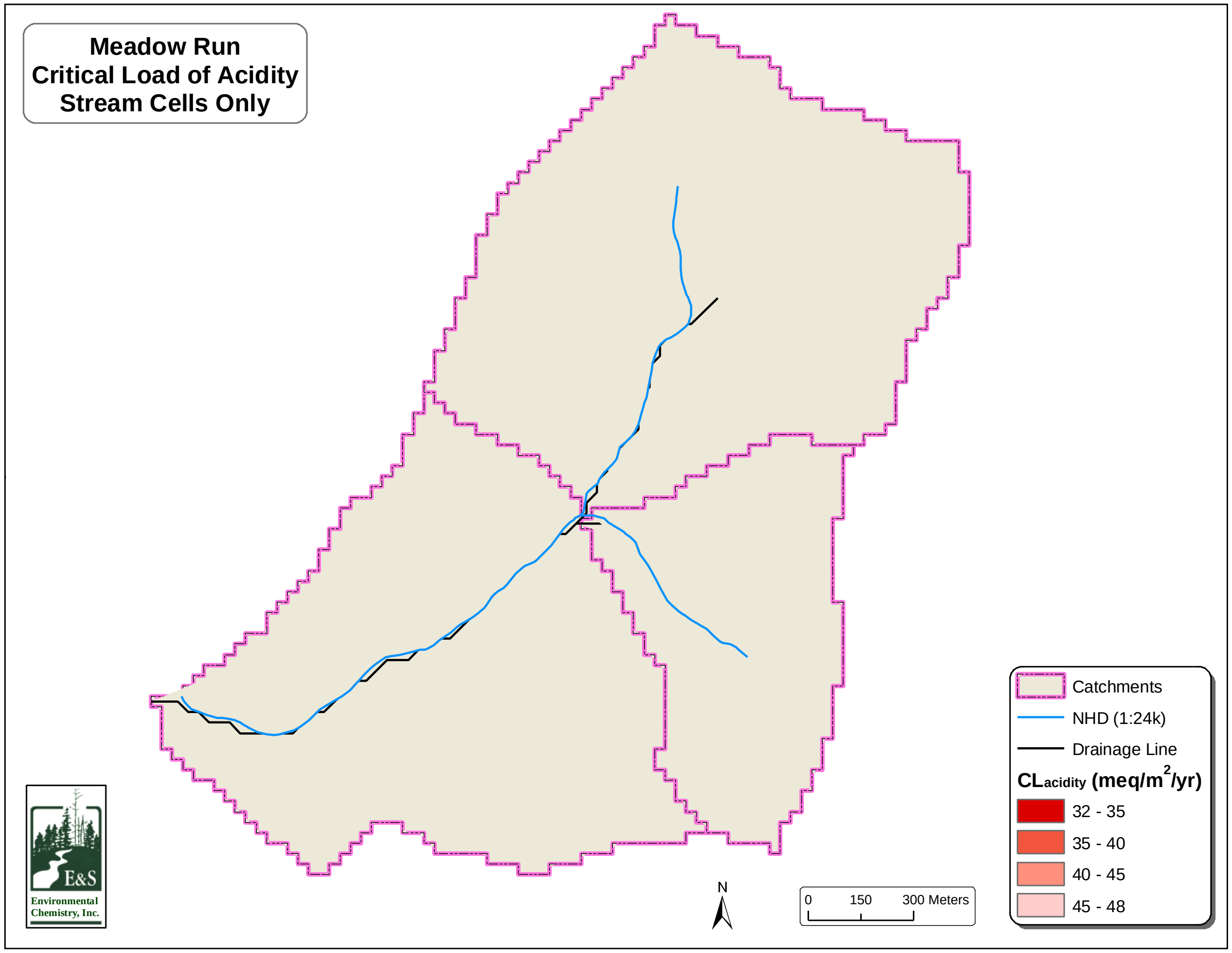


Figure 29. Extraction of CL for stream cells only from among all 30-m cells within the Meadow Run watershed in Shenandoah National Park. Stream cell locations were determined by assumed water flow paths from cell to cell according to topography generated from the DEM. This step is necessary in order to transfer results of CL calculation for the watershed to the stream locations determined in the NHD. The average calculated CL from among the stream cells depicted here was assigned to NHD streams that occur within this watershed, which are indicated here with a blue line. Synthetic streams, determined from the apparent drainage pattern, closely approximated NHD stream locations.

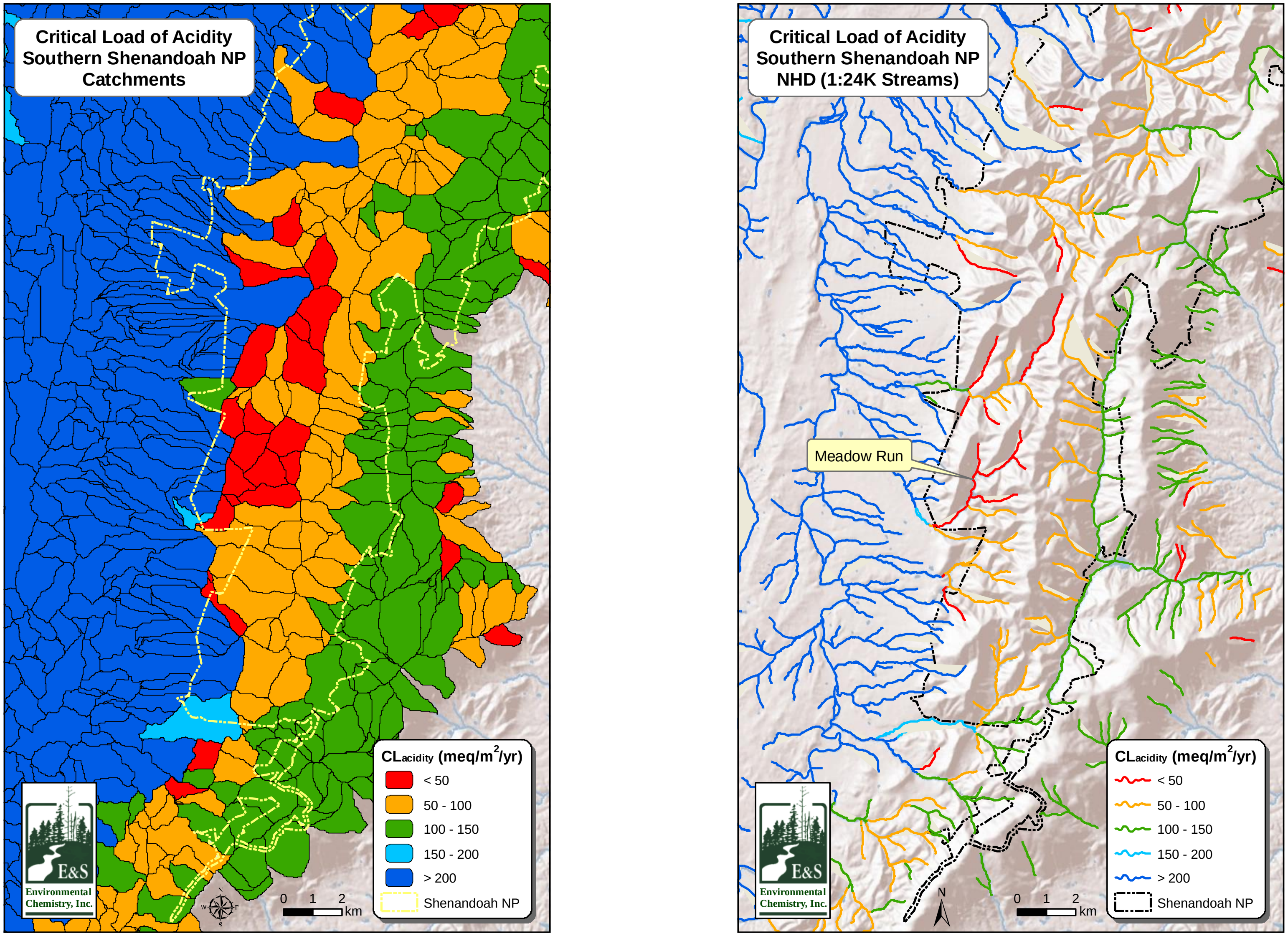


Figure 30. Calculated CL of acidity to protect against ANC below 20 μeq/L for watersheds in and around the southern portion of Shenandoah National Park, based on watersheds (left column) and stream reaches (right column).

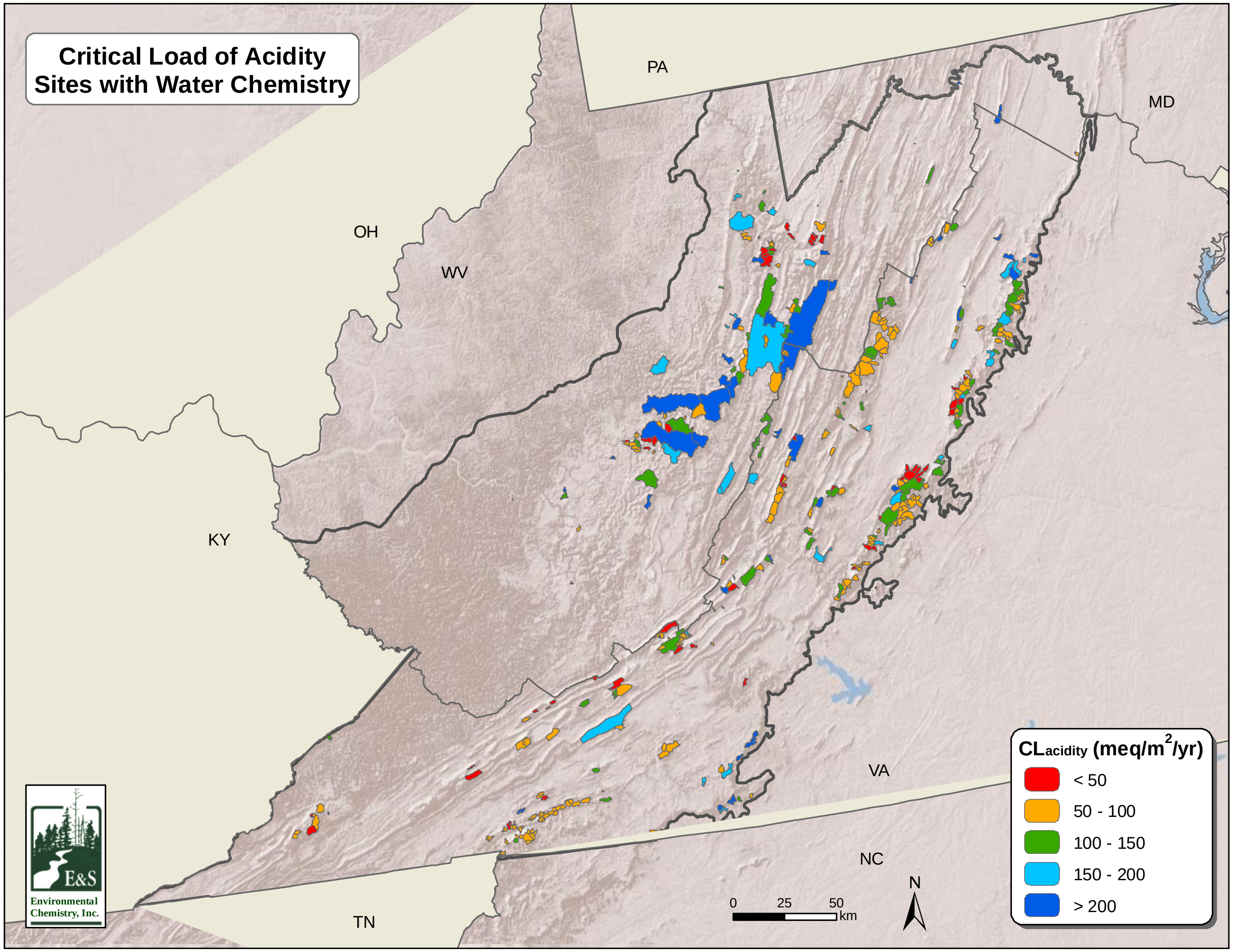


Figure 31. Results of calculations for CL of acidity to prevent ANC from going below 20 µeq/L for all watersheds (n=522) having stream chemistry, using algorithms for calculating BC_w that were based on relationships with water chemistry plus landscape characteristics.

Examples are shown in Figures 32 and 33 for southern Shenandoah National Park in Virginia and the area around Otter Creek and Dolly Sods Wilderness areas in West Virginia, illustrating different CL results based on varying levels of data specificity. The right panel in each of these figures shows the primary site-specific CL results calculated using BC_w estimates taken directly from MAGIC. For the respective middle panels, BC_w was calculated using stream chemistry plus mappable watershed attributes (the secondary site-specific results). Note that the watershed sizes shown in the right and middle panels were determined by the locations of the stream samples. The left panels reflect results for the topographically determined watersheds that were calculated based on topography (mapped regional results). These tend to be smaller than the watersheds defined by the stream sampling locations. Thus, the topographically determined watersheds provide a higher resolution depiction of CL than do the sampled watersheds. Results of the CL calculations for the mapped regional approach are more uncertain because they are based on regression equations that included only landscape variables. Nevertheless, the patterns in the calculated CL are similar, regardless of approach.

Overall, CL calculations using SSWC were similar across the three methods of estimating BC_w. Critical load calculations using the regression equations to predict BC_w, based on the secondary site-specific results and based on mapped regional results, yielded reasonable agreement with primary site-specific CL calculations using MAGIC estimates of BC_w (Figure 34). Nevertheless, results of regression estimates more closely matched MAGIC estimates in the Blue Ridge ecoregion than in the other two ecoregions investigated.

3.6 Length of Stream in Various Critical Load Classes

Results of CL calculations were expressed across the entire stream network within the study area. This allowed data to be reported statistically and to be mapped as a continuous function, rather than discrete points along the stream. Thus, results are expressed on the basis of stream length.

For the study area as a whole, about 32 to 38% of the stream length (depending on selection of threshold ANC value) was classified as having CL above 200 meq/m^2/yr (Figure 35; Table 5). The remainder of the stream length had lower calculated CL values, with 22% to 43% of the stream length having CL below 100 meq/m^2/yr. For most CL classes, there was not much difference in the extent of stream length within the class as influenced by the threshold ANC value selected. For the lowest CL class, however (less than 50 meq/m^2/yr), choice of threshold ANC value made a substantial difference to the stream length calculations. The length of stream estimated to have

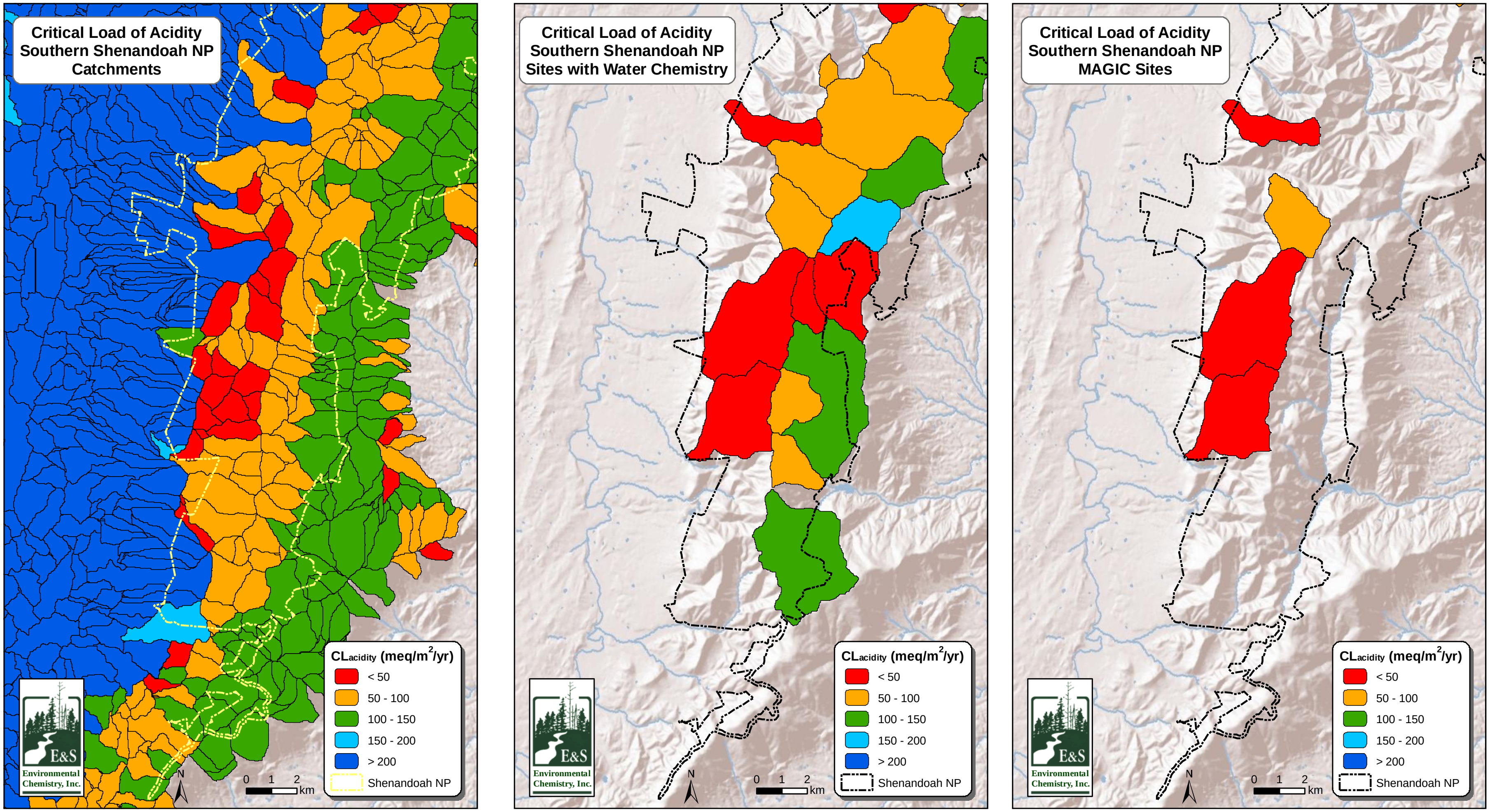


Figure 32. Comparisons among modeling approaches for calculating CL of acidity to prevent ANC from going below 20 μeq/L for watersheds in and around the southern portion of Shenandoah National Park. Calculations are based on: direct MAGIC model estimates of weathering (available for 4 watersheds only; right panel), watersheds for which there exists water chemistry data (20 watersheds; middle panel), and all watersheds (left panel). Watershed boundaries were determined by sampling site locations for the right and center panels, and by inter-pixel flow accumulation for the left panel. Spatial patterns in CL are similar using the three approaches.

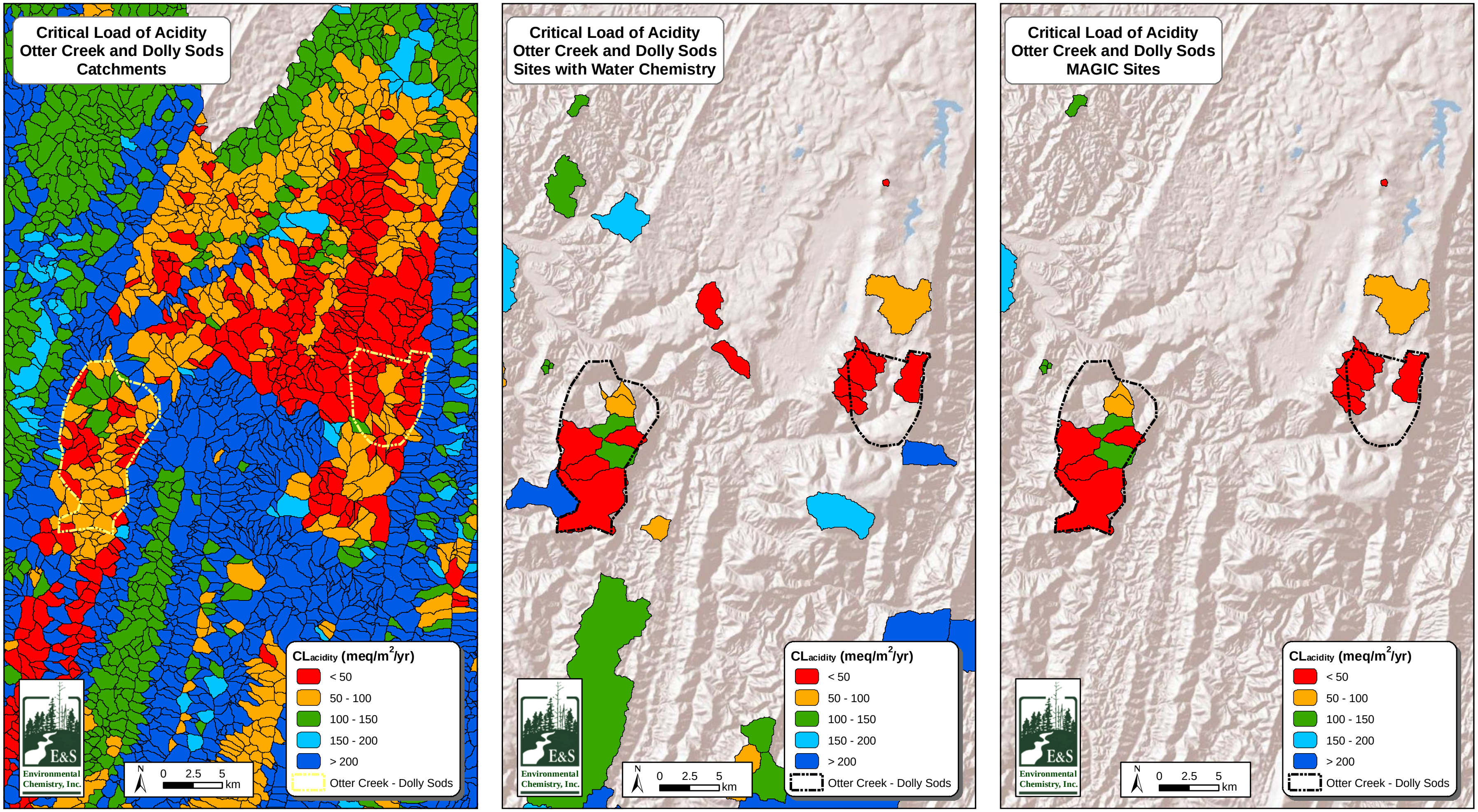


Figure 33. Comparisons among modeling approaches for calculating CL of acidity to prevent ANC from going below 20 µeq/L for watersheds in and around the Otter Creek/Dolly Sods Wilderness areas. Calculations are based on: direct MAGIC model estimates of weathering (available for ~13 watersheds only; right panel), watersheds for which there exists water chemistry data (~ 30 watersheds; middle panel), and all watersheds (left panel). Watershed boundaries were determined by sampling site locations for the right and center panels, and by inter-pixel flow accumulation for the left panel. Spatial patterns in CL are similar using the three approaches.

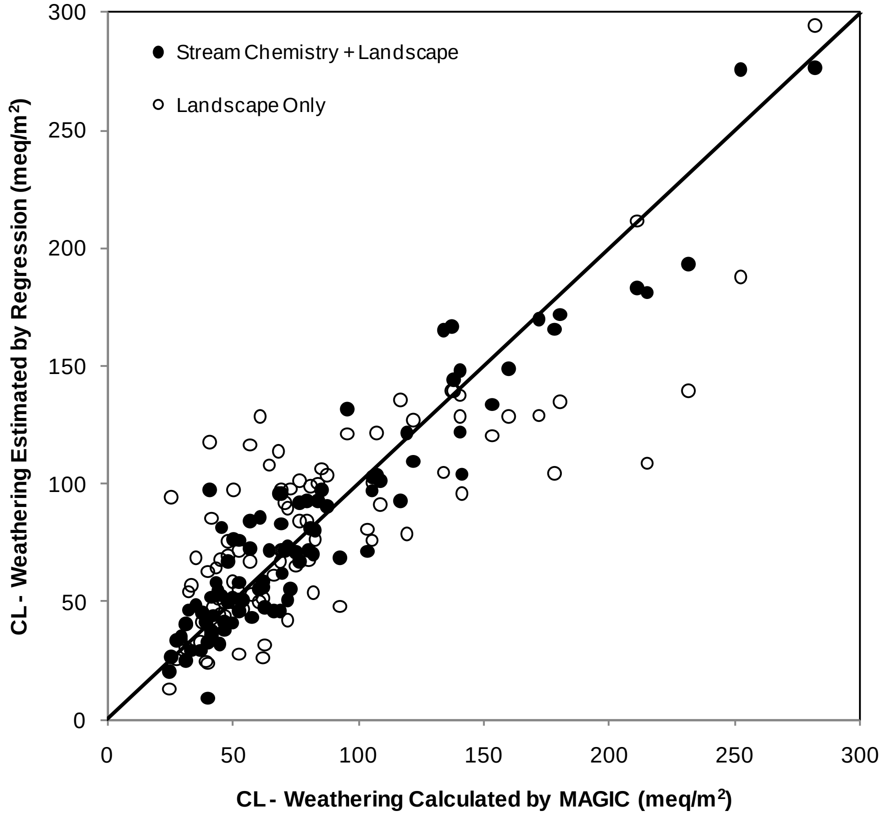
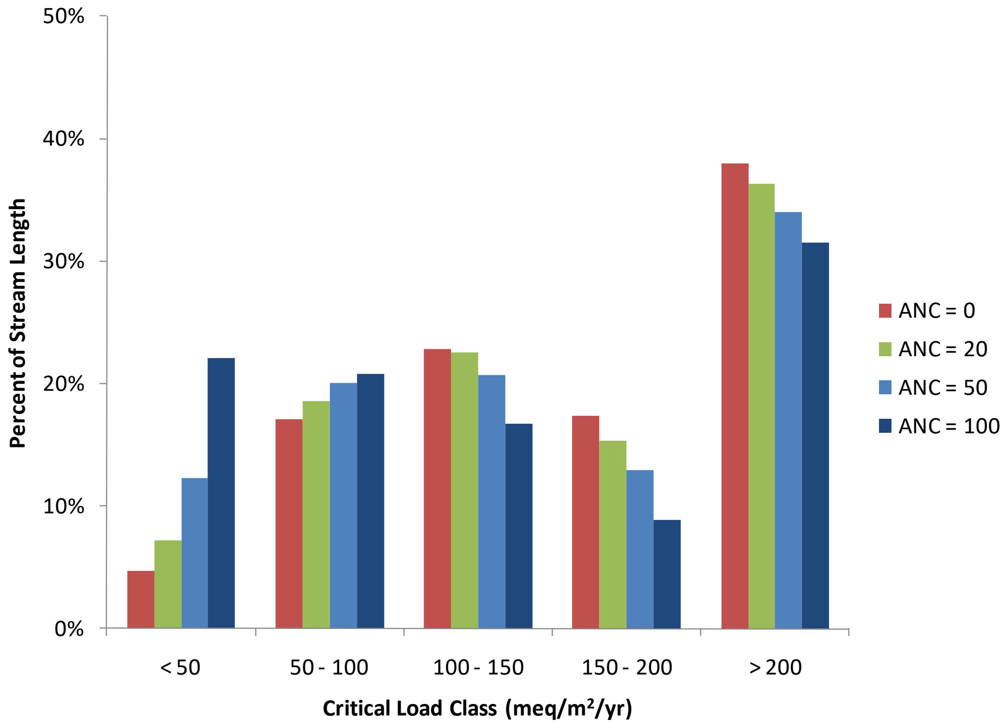


Figure 34. Critical load calculations for the 92 sites modeled with MAGIC. The CL calculations using SSWC, where weathering was calculated with MAGIC, are shown on the x-axis. SSWC CL calculations, where weathering was estimated using regression equations (water chemistry plus landscape data; or landscape data alone), are shown on the y-axis. One outlier was deleted; it was influenced by a small section of carbonate lithology at the stream outlet.



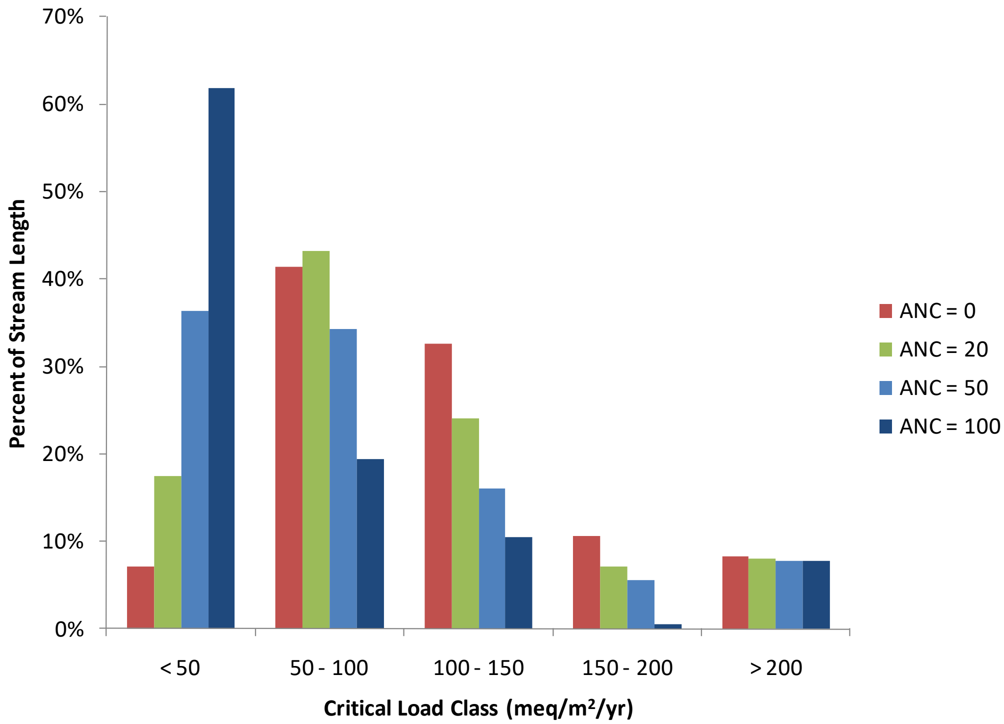


Figure 35. Percent of stream length in various CL classes based on SSWC estimates of critical load of acidity to protect against streamwater ANC below 0, 20, 50, and 100 μeq/L. Results are presented for the entire study area (top panel) and for designated Wilderness areas within the study area (bottom panel).

Table 5. Length and percent of streams within the study region in different CL classes.

Critical ANC Criterion (μeq/L)	Ecoregion	Length (km) and (Percent) of Streams within CL Class (meq/m²/yr)				
		<50	50-100	100-150	150-200	>200
0	Blue Ridge.	379 (3%)	8,920 (67%)	3,136 (24%)	287 (2%)	525 (4%)
	Ridge & Valley	1,136 (2%)	5,821 (9%)	14,077 (22%)	10,003 (16%)	31,742 (51%)
	Central Appalachian	4,129 (9%)	5,783 (13%)	10,128 (23%)	10,570 (24%)	13,342 (30%)
20	Blue Ridge	1,462 (11%)	9,010 (68%)	2,149 (16%)	101 (1%)	535 (4%)
	Ridge & Valley	1,915 (3%)	6,821 (11%)	14,354 (23%)	8,358 (13%)	31,331 (50%)
	Central Appalachian	5,265 (12%)	6,435 (15%)	10,561 (24%)	9,966 (23%)	11,724 (27%)
50	Blue Ridge	4,436 (33%)	7,113 (54%)	1,125 (8%)	57 (0%)	527 (4%)
	Ridge & Valley	3,156 (5%)	9,161 (15%)	12,943 (21%)	6,712 (11%)	30,806 (49%)
	Central Appalachian	7,132 (16%)	7,795 (18%)	10,807 (25%)	8,733 (20%)	9,485 (22%)
100	Blue Ridge	9,301 (70%)	3,036 (23%)	383 (3%)	16 (0%)	521 (4%)
	Ridge & Valley	6,545 (10%)	11,960 (19%)	9,338 (15%)	4,483 (7%)	30,453 (49%)
	Central Appalachian	10,705 (24%)	9,964 (23%)	10,330 (24%)	6,115 (14%)	6,837 (16%)
0	Study Region	5,644 (5%)	20,524 (17%)	27,341 (23%)	20,860 (17%)	45,619 (38%)
20		8,642 (7%)	22,267 (19%)	27,064 (23%)	18,425 (15%)	43,590 (36%)
50		14,725 (12%)	24,070 (20%)	24,874 (21%)	15,502 (13%)	40,817 (34%)
100		26,551 (22%)	24,960 (21%)	20,052 (17%)	10,614 (9%)	37,811 (32%)

CL ≤ 50 meq/m²/yr varied by more than a factor of four, depending on which threshold ANC value was selected.

The breakdown of stream length by CL class was quite different for the portions of the study area in designated Wilderness (Figure 35, top panel) as compared with the study area as a whole (Figure 35, bottom panel). Critical loads were generally much lower and more heavily influenced by selection of the threshold ANC value for designated Wilderness streams as compared with non-Wilderness streams. Over 60% of the Wilderness stream length had CL less than 50 meq/m²/yr to protect to stream ANC above 100 μeq/L. About 70% of the Wilderness stream length had CL less than 100 meq/m²/yr to protect to stream ANC above 50 μeq/L. Nearly half of the Wilderness stream length had CL less than 100 meq/m²/yr to protect to stream ANC above zero.

Thus, selection of the threshold ANC value (0, 20, 50, or 100 μeq/L) seems to have more influence on calculation of the CL in Wilderness areas versus the region as a whole. In particular,

choice of the threshold ANC value had a large effect on the resulting CL for the most acid-sensitive (CL ≤ 50 meq/m^2/yr) stream watersheds in Wilderness settings.

3.7 Critical Load Exceedance

The final step in the CL process is calculation of CL exceedance. This step identifies portions of the landscape where ambient S plus N deposition acidity exceeds the long-term steady state CL. To perform this calculation, total wet plus dry S and N deposition was calculated based on five-year averages of NADP wet (Grimm interpolation) and Community Multiscale Air Quality (CMAQ) model dry deposition centered on the year 2002 (Figures 36 and 37). Total N + S deposition acidity was then processed with the continuous upslope averaging function. Values along topographically determined stream pixels were extracted and averaged on a watershed basis in the same manner that the pixel-by-pixel CL estimates were coded to the watersheds. These watershed averaged values of total ambient deposition of acidity were then overlayed with the CL maps to generate regional estimates of CL exceedance, or areas where ambient deposition exceeds the CL. These are shown in Figures 38-40 for the critical ANC criteria values 20, 50, and 100 μeq/L, respectively (Appendix E shows the CL exceedance map for the ANC criterion value of 0 μeq/L). Broad areas of the study region were found to be in CL exceedance (Table 6). Such areas are disproportionately associated with Class I areas and other public lands. This is largely because public land in the study area tends to be located at relatively high elevation on relatively sensitive geology, and therefore receives higher deposition, and has higher runoff, lower BC_w, and lower Bc_{up}, as compared with lands located at lower elevations and on less sensitive geologies.

About half of the stream length within the study region was calculated to receive current acidic deposition in exceedance of the CL to protect against stream ANC below zero. That percentage increased to between 53% and 63% for the threshold ANC values of 20, 50, and 100 μeq/L. Nearly one-fourth of the stream length in the study region was estimated to be receiving acidic deposition that is more than double the CL for protecting stream ANC from going below 50 μeq/L. Exceedance of the CL was most prevalent in the Blue Ridge ecoregion, followed by the Central Appalachian ecoregion. Streams found to be in exceedance were about 6 times more prevalent in the Blue Ridge ecoregion as compared with the Central Appalachian ecoregion, and about 12 times more prevalent in the Blue Ridge ecoregion as compared with the Ridge and Valley ecoregion.

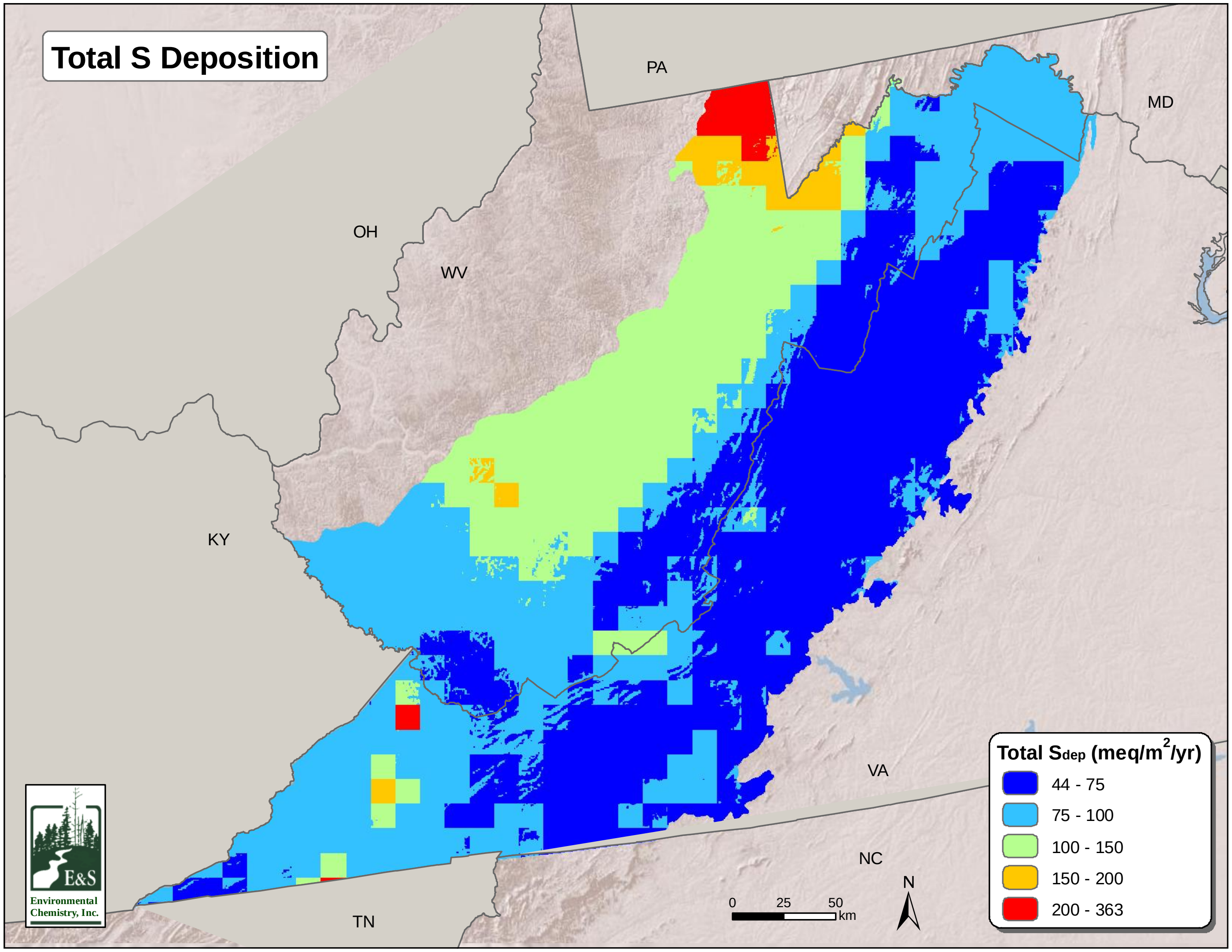


Figure 36. Regional patterns in total S deposition, based on interpolated NADP wet deposition averaged over a five year period centered on 2002 and CMAQ model estimates of dry deposition for 2002. Note that S deposition in units of kg S/ha/yr is equal to S deposition in units of meq/m^2/yr times 0.16.

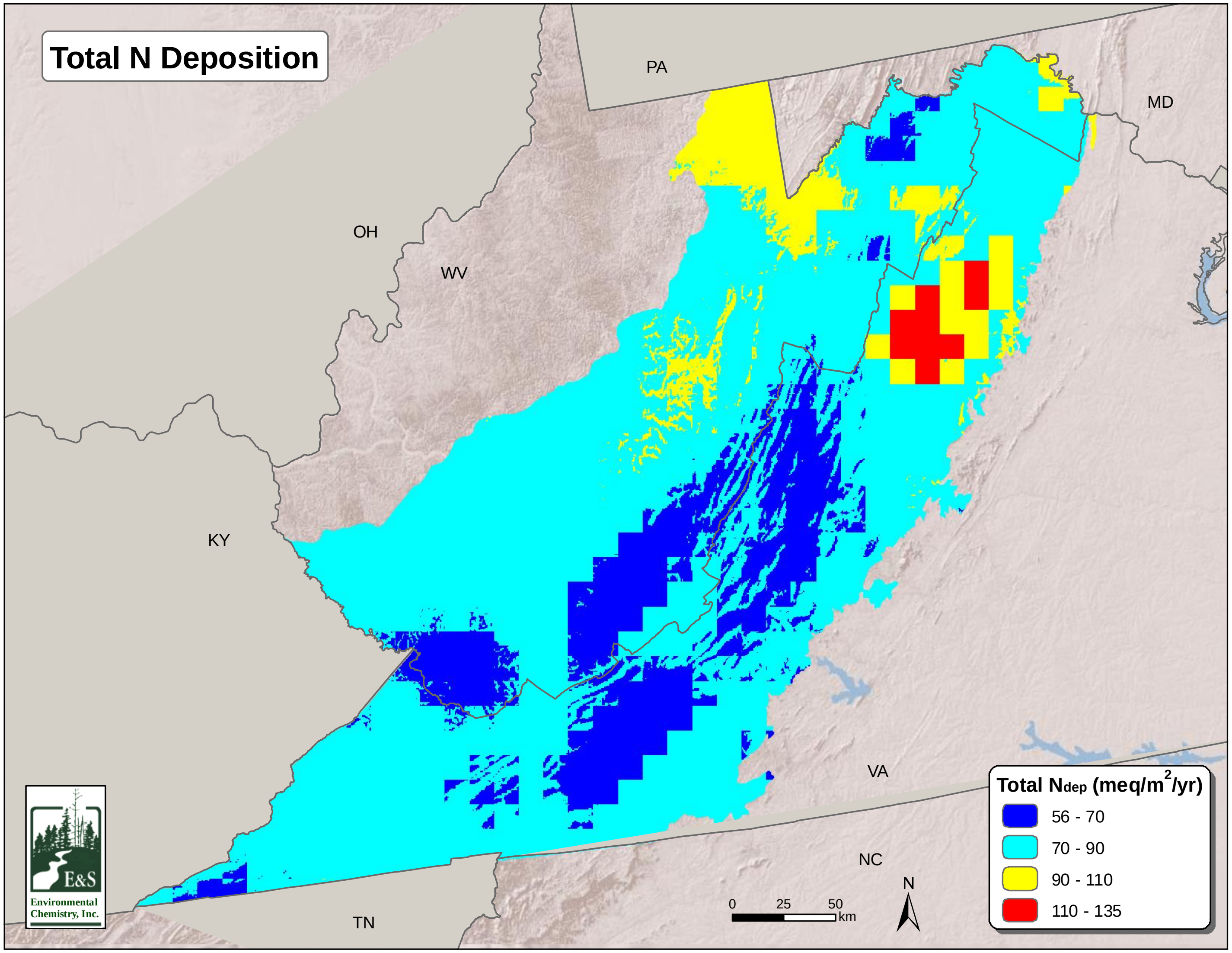


Figure 37. Regional patterns in total N deposition, based on interpolated NADP wet deposition averaged over a five-year period centered on 2002 and CMAQ model estimates of dry deposition for 2002. Note that N deposition in units of kg N/ha/yr is equal to N deposition in units of meq/m^2/yr times 0.14.

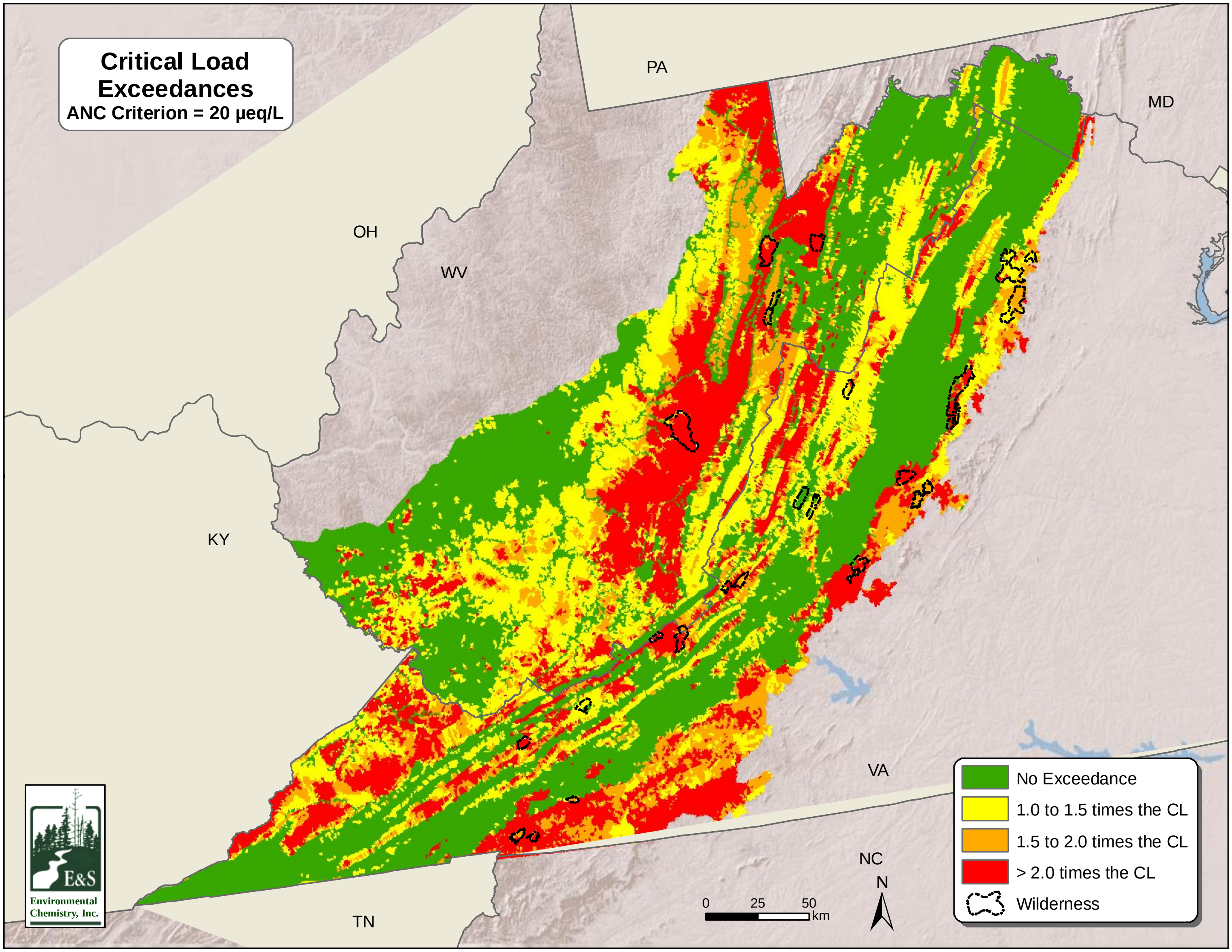


Figure 38. Critical load exceedance map for the ANC criterion 20 µeq/L.

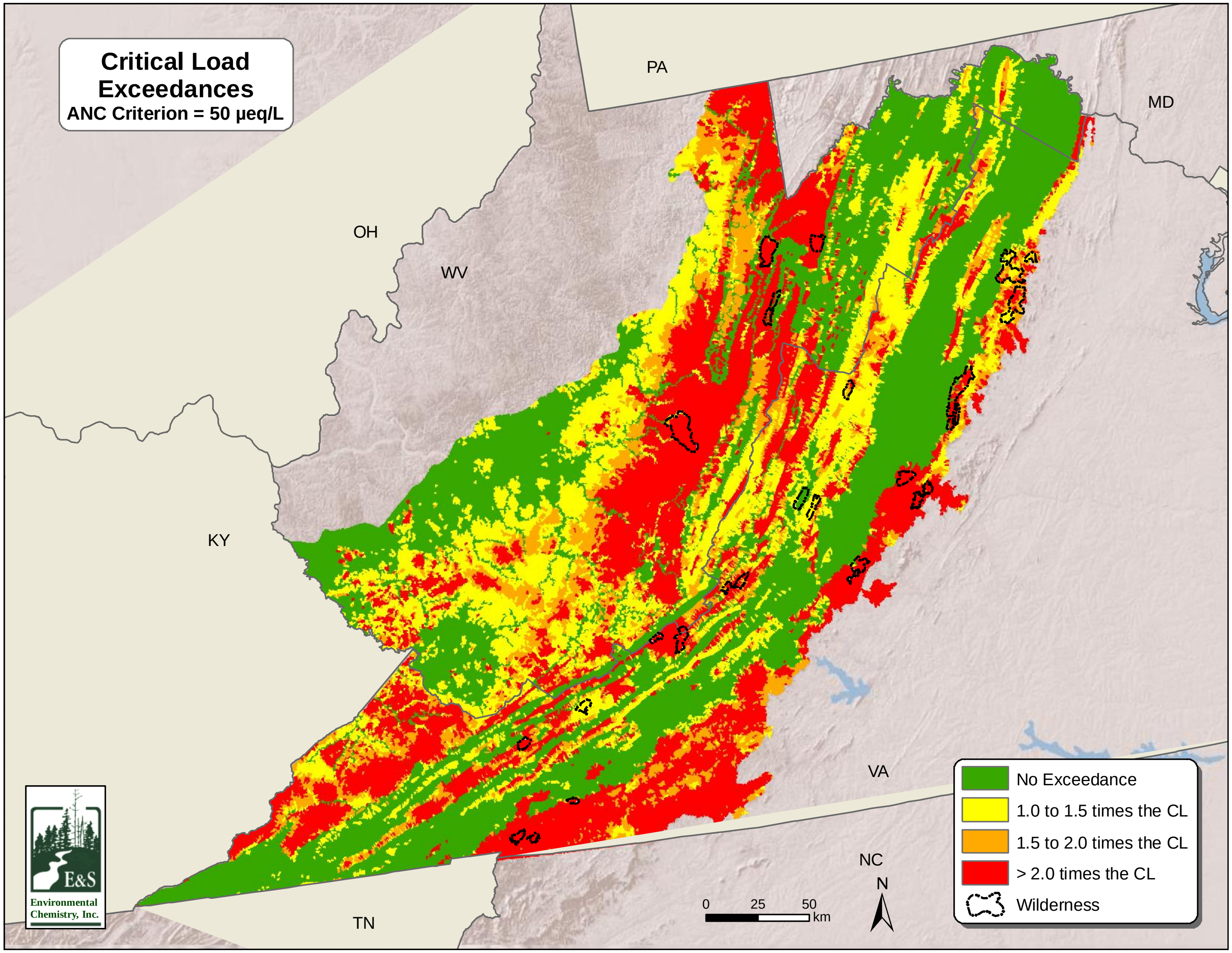


Figure 39. Critical load exceedance map for the ANC criterion 50 µeq/L.

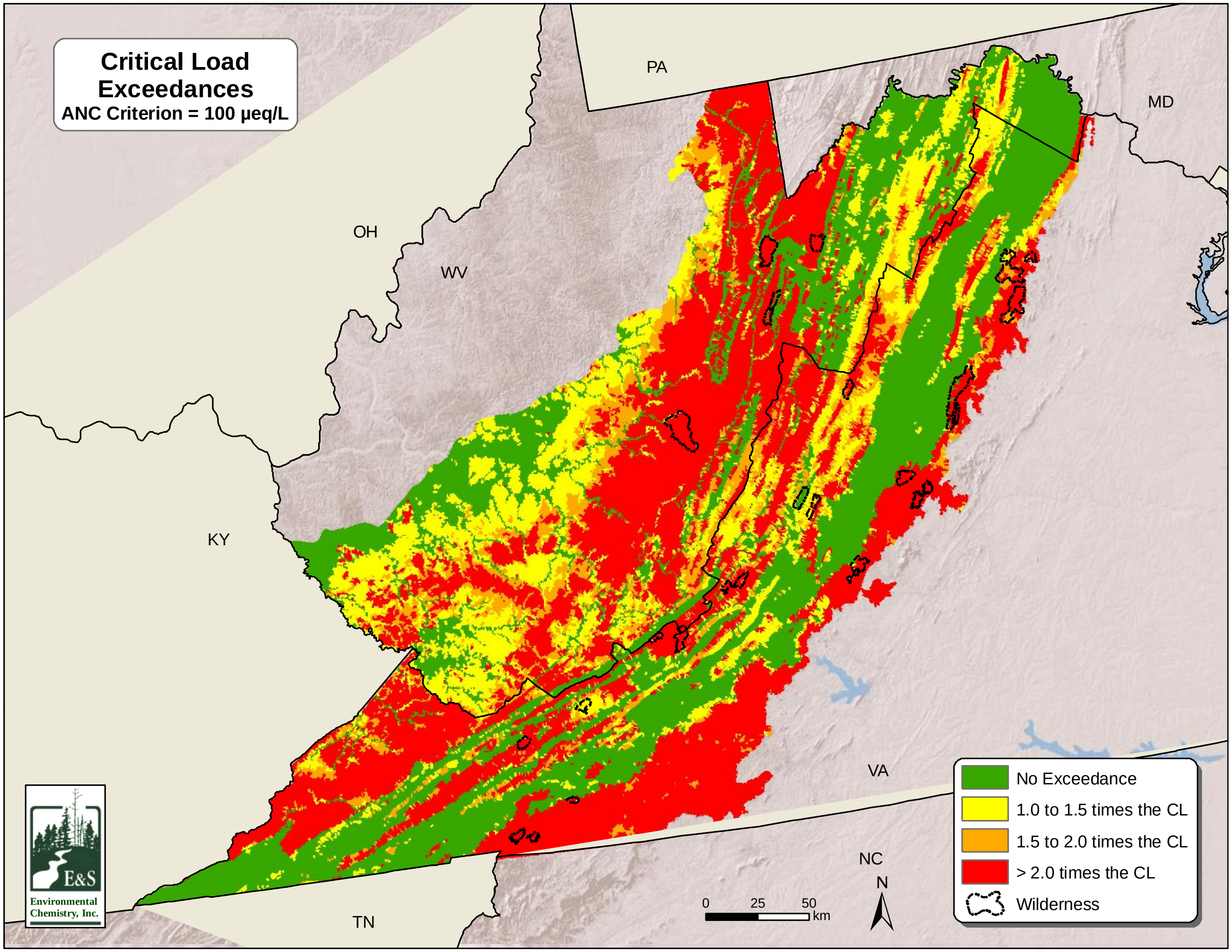


Figure 40. Critical load exceedance map for the ANC criterion 100 μeq/L.

Table 6. Length and percent of stream length within the study region in CL exceedance.

Critical ANC Criterion (μeq/L)	Ecoregion	Length (km) and (Percent) of Stream Length within Exceedance Class			
		Not in Exceedance	1.0 to 1.5 Times the CL	1.5 to 2.0 Times the CL	> 2.0 Times the CL
0	Blue Ridge	758 (6%)	3,921 (25%)	5,682 (43%)	3,523 (27%)
	Ridge & Valley	41,801 (67%)	13,188 (21%)	4,585 (7%)	3,203 (5%)
	Central Appalachian	17,840 (41%)	12,998 (30%)	4,592 (10%)	8,517 (19%)
20	Blue Ridge	651 (5%)	2,081 (16%)	4,308 (32%)	6,217 (47%)
	Ridge & Valley	39,884 (64%)	12,915 (21%)	5,394 (9%)	4,585 (7%)
	Central Appalachian	15,819 (36%)	12,731 (29%)	5,254 (12%)	10,148 (23%)
50	Blue Ridge	610 (5%)	979 (7%)	2,223 (17%)	9,442 (71%)
	Ridge & Valley	37,773 (60%)	12,202 (19%)	5,580 (9%)	7,222 (12%)
	Central Appalachian	13,188 (30%)	11,598 (26%)	6,437 (15%)	12,726 (29%)
100	Blue Ridge	546 (4%)	285 (2%)	691 (5%)	11,737 (89%)
	Ridge & Valley	34,717 (55%)	10,136 (16%)	5,811 (9%)	12,115 (19%)
	Central Appalachian	8,936 (20%)	10,311 (23%)	6,150 (14%)	18,554 (42%)
0	Study Region	60,399 (50%)	29,478 (25%)	14,859 (12%)	15,242 (13%)
20		56,355 (47%)	27,727 (23%)	14,955 (12%)	20,950 (17%)
50		51,571 (43%)	24,779 (21%)	14,240 (12%)	29,389 (24%)
100		44,199 (37%)	20,731 (17%)	12,652 (11%)	42,406 (35%)

3.8 Time to Steady State

The SSWC model estimates the long-term steady-state CL that is expected to allow acidified streams to recover to a designated critical ANC criterion value. No information is provided, however, regarding the amount of time that it may take to affect resource recovery at that CL deposition level. To address this uncertainty, the time to reach steady-state condition was simulated using the MAGIC model at each of the 92 calibration sites. Dynamic responses for the SSWC CL for each stream water criterion were examined.

The calibrated weathering in MAGIC for each site was used in the SSWC model to calculate the CLs for that site for each water quality index value. It is expected, therefore, that a long-term simulation using calibrated MAGIC driven by the SSWC CL should converge on the water quality index value. The time to reach this steady-state value can be extracted from the

MAGIC simulations. Simulations were run for 1000 years at each site starting in 1995 (the calibration year for the modeled sites) and using the protocol described below.

The future deposition of base cations and Cl^- for the MAGIC simulations were assumed to be constant at their 1995 values for the entire 1000 year period. Deposition of SO_4^{2-}, NO_3^-, and NH_4^+ were varied from 1995 to 2007 according to the observed linear trend in wet deposition of each ion at each site using the approach of Grimm et al. (1997) to interpolate observed NADP data during that period. From 2007 to 2010, deposition of S and N were varied according to projected atmospheric deposition, given current emissions control policies. Starting in 2010 and finishing in 2020, the SSWC CL for each site was implemented linearly over the 10 year period. The acidity of deposition was increased or decreased to the SSWC CL value. From 2020 to the end of the 1000 year simulation, the deposition of acidity was held constant at its SSWC CL value.

The 1000-year simulations provided time-series of simulated future calculated ANC values for each critical ANC threshold at each site. The simulation period from 1995 to 2020 was driven by deposition sequences unrelated to the SSWC CL, so that time period was ignored. The SSWC CLs were fully implemented in each simulation by 2020, so the first year examined for dynamic responses of the outputs was chosen to be 2025. Starting in 2025, the simulated time series were sampled every 25 years for the first 300 years, then every 50 years for the next 300 years, and then every 100 years for the final 300 years.

In all cases, the simulations approached the critical water quality index in an asymptotic manner, from either above or below depending on the value of calculated ANC prior to implementation of the SSWC CL. It was necessary, therefore, to define the achievement of "steady-state" in the simulations as the point in the time series when the simulated value approached within some specified distance from the nominal value. This interval was chosen as 2.0 μeq/L for this study.

Results of these time-to-steady-state analyses (Figure 41) suggested that:

- most of the modeled watersheds will not reach steady state for hundreds of years, and
- the time period is somewhat longer if the selected threshold ANC value is higher (more protective).

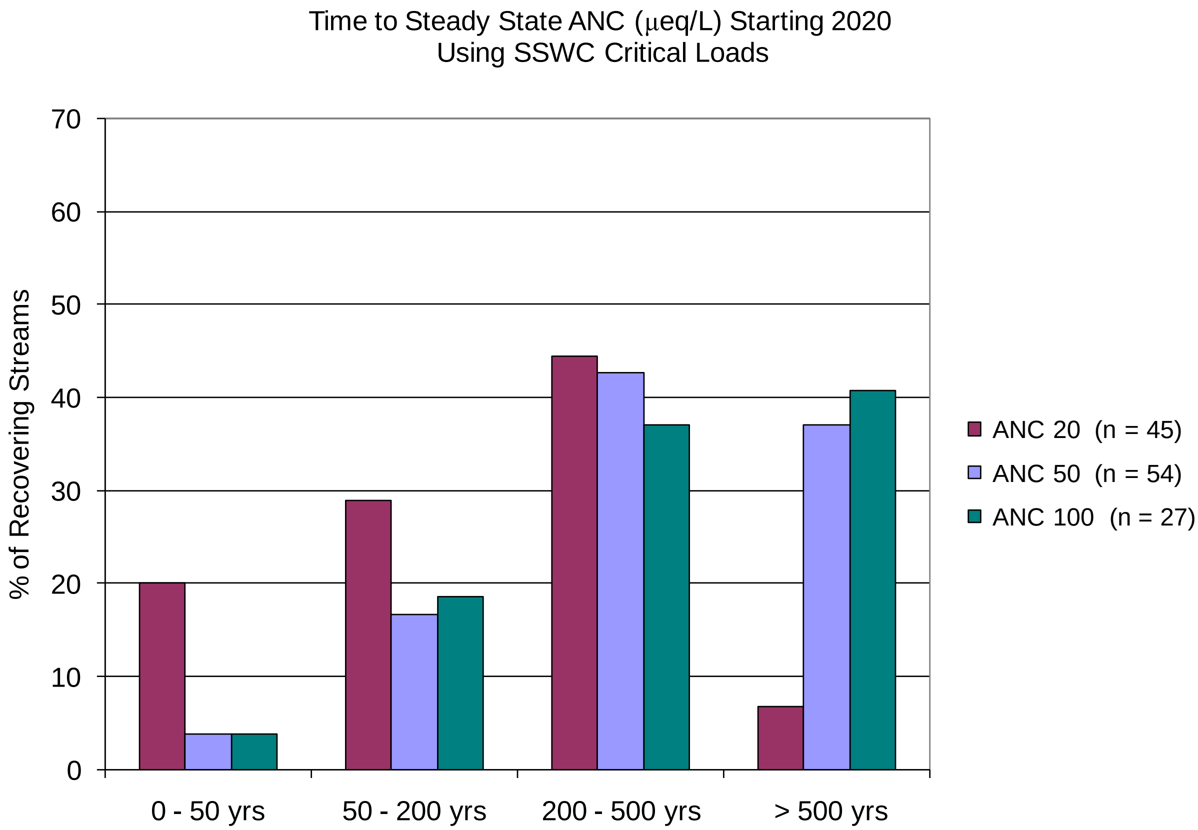


Figure 41. Breakdown for the previously impacted modeled streams (those having current ANC below the respective critical ANC threshold values) of modeled time to reach steady state under continued deposition at the CL level. Three critical ANC criteria thresholds are illustrated: 20, 50, and 100 µeq/L.

The relationships between CL, selection of ANC criterion value, and selection of evaluation year are important. Higher CLs can be tolerated if one only wishes to protect against acidification to the year 2050, as compared with more stringent deposition reductions required to protect systems against acidification for a longer period of time. More substantial emissions and deposition reductions are needed to affect recovery of damaged systems within a short period of time as opposed to a longer period of time. Higher CLs are allowable if one wishes to prevent acidification to ANC = 0 µeq/L (chronic acidification) than if one wishes to be more protective and prevent acidification to ANC below 20 µeq/L (possible episodic acidification) or below 50 or 100 µeq/L (general biological health). Thus, use of these CL calculations for decision making requires an understanding that the majority of the modeled watersheds will likely not come into steady state with the SSWC CL deposition values for more than 200 years.

4.0 DISCUSSION

4.1 Weathering Estimates

A computationally efficient and robust method for estimating BC_w on a continuous basis across a regional landscape was developed. It was based on weathering estimates extracted from a well-tested process-based watershed model of drainage water acid-base chemistry and also on features of the landscape that are available as regional spatial data coverages and that are known to correlate with acid sensitivity.

Results indicate substantial spatial variability in weathering estimates across the study region (Figure 18). Weathering estimates were especially low (less than 50 meq/m^2/yr) in portions of the Blue Ridge ecoregion, including the southern section of Shenandoah National Park in Virginia and portions of the Central Appalachian ecoregion, including much of Otter Creek and Dolly Sods Wilderness areas in West Virginia.

Predictive ability was greater for sites with water chemistry as compared with calculations using landscape variables only (Table 3). Nevertheless, predictive equations developed using only regionally available landscape variables explained 64% to 85% of the variation in simulated weathering derived from the process model. This process provides an approach, with quantifiable uncertainty, for estimating weathering using calibration results from a well-tested process model. Other common methods for estimating BC_w for input into SSWC and other steady state CL models are based on empirical equations with no basis for assessing uncertainty. In addition, the utilization of readily available spatial datasets (i.e., elevation, soil characteristics, lithology), combined with site-specific process modeling to predict weathering on a 30-m grid cell basis, allows for this method of estimating base cation weathering to be extrapolated to a large region and perhaps to be transferred to other regions of the United States.

In general, the independent variables included in the regression equations (Table 3) were logical products of current understanding of catchment weathering and acid-base chemistry. Equations to predict weathering at sites for which stream chemistry data were available consistently selected either SBC in stream water or streamwater calculated ANC as primary predictor variables. In two of the three ecoregions, stream NO_3^- was also selected. This suggests that weathering co-varies to some extent with N leaching. The reason(s) for this are unclear. Weathering estimates increased in all cases with increasing SBC, calculated ANC, and NO_3^- concentration. For those weathering equations that included stream chemistry variables, none of the geologic sensitivity or soil variables were selected for inclusion in the regression equations.

This is likely because stream chemistry effectively integrates soil and geologic condition, and may in fact provide a better reflection of base cation supply than available spatial data on geology and soils.

Equations to predict weathering at sites lacking stream chemistry data in all cases selected soil and/or geologic variables as independent variables. Weathering increased with increasing coverage of carbonate, felsic, and mafic lithologies, but decreased with increasing siliciclastic lithology. This result agrees with geological sensitivity mapping conducted in this region by Sullivan et al. (2007). Weathering increased with decreasing soil depth in the Blue Ridge ecoregion, a counter-intuitive result that may have been driven by cross-correlation with other variables. Weathering decreased, as expected, with increasing soil pH and decreasing soil clay content. Other landscape variables included in the regression equations and their signs (positive or negative) included watershed area (+), elevation (-), and average watershed slope (-). All of these variables, and their signs, agree with current scientific understanding of acidification sensitivity. The most acid-sensitive streams (lowest BC_w) tend to be located in small watersheds, at high elevation, on steep slopes.

The CL calculations using SSWC were similar regardless of which of the three methods of estimating BC_w was used. Critical load calculations using the regression equations to predict BC_w, based on secondary site- specific results (including water chemistry plus landscape characteristics) and also those based on mapped regional results, yielded reasonable agreement with CL calculations using MAGIC estimates of BC_w (Figure 34). Nevertheless, it is important to note that the weathering and CL maps reported here are preliminary maps, not final maps. This project demonstrated one particular technique for estimating weathering. It is based on a well-tested and widely used process-based model. However, there has not been a formal uncertainty analysis, and the confidence in these estimates is unknown. It will be important to continue research efforts to quantify BC_w, the most important and most uncertain variable in CL calculations reported here (cf., McDonnell et al. in review)

4.2 Critical Load and Exceedance Levels

Overall, the calculated CL values were relatively low throughout the study area, especially in the Blue Ridge ecoregion. A third of the stream length in that ecoregion had CL to maintain ANC above 50 μeq/L less than 50 meq/m^2/yr, and 87% of the stream length in the Blue Ridge had CL less than 100 meq/m^2/yr for protection to ANC above 50 μeq/L. For the entire

study area, 32% of the stream length exhibited CL (to maintain ANC above 50 μeq/L) below 100 meq/m^2/yr (Table 5). As a consequence of these low calculated CL values, coupled with relatively high levels of acidic deposition (Figure 42), much of the land within the study region was calculated to be in exceedance of the CL. Depending on selection of ANC threshold, 50% to 63% of the stream length within the region was calculated to be in CL exceedance (Table 6). This result suggests the possibility of long-term impacts on aquatic ecosystem health under sustained acidic deposition at levels near current values.

4.3 Temporal Pattern of Response

The CL and CL exceedance values calculated in this project pertain to long-term, steady-state water quality conditions as defined in the algorithm used in the SSWC model. It is known that it may take decades or centuries to reach the steady-state condition with respect to deposition acidity and stream chemistry. Land managers may prefer to affect recovery of damaged stream watersheds within a shorter time period. Conversely, managers may be willing to accept deposition levels that eventually will cause damage but not for a very long time. Thus, the steady state CL and exceedance calculations may not provide managers with all of the information needed to make informed land management decisions. To address this uncertainty, the time to reach the steady-state CL condition was simulated using the MAGIC model at the 92 dynamic calibration sites. Simulations were run for 1000 years at each site after setting the future deposition acidity to the SSWC CL value for each stream threshold criterion at each site.

The results of this dynamic analysis showed clearly that relationships between SSWC CL value, selection of stream ANC criterion value, and selection of evaluation year are important. More substantial emissions and deposition reductions (below that of the SSWC CL) are needed to affect recovery of damaged systems within a short period of time (decades) as opposed to longer periods of time (centuries). The longer one is willing to wait for recovery, the more relevant is the SSWC CL estimate to actual recovery achieved. For the dynamic modeling sites in this pilot study region, the simulations suggest that it can take hundreds of years to reach specified stream water ANC criteria assuming atmospheric deposition of acidity at the SSWC long-term steady-state CL level. The use of these SSWC CL calculations for decision making requires an understanding of this dynamic aspect of recovery.

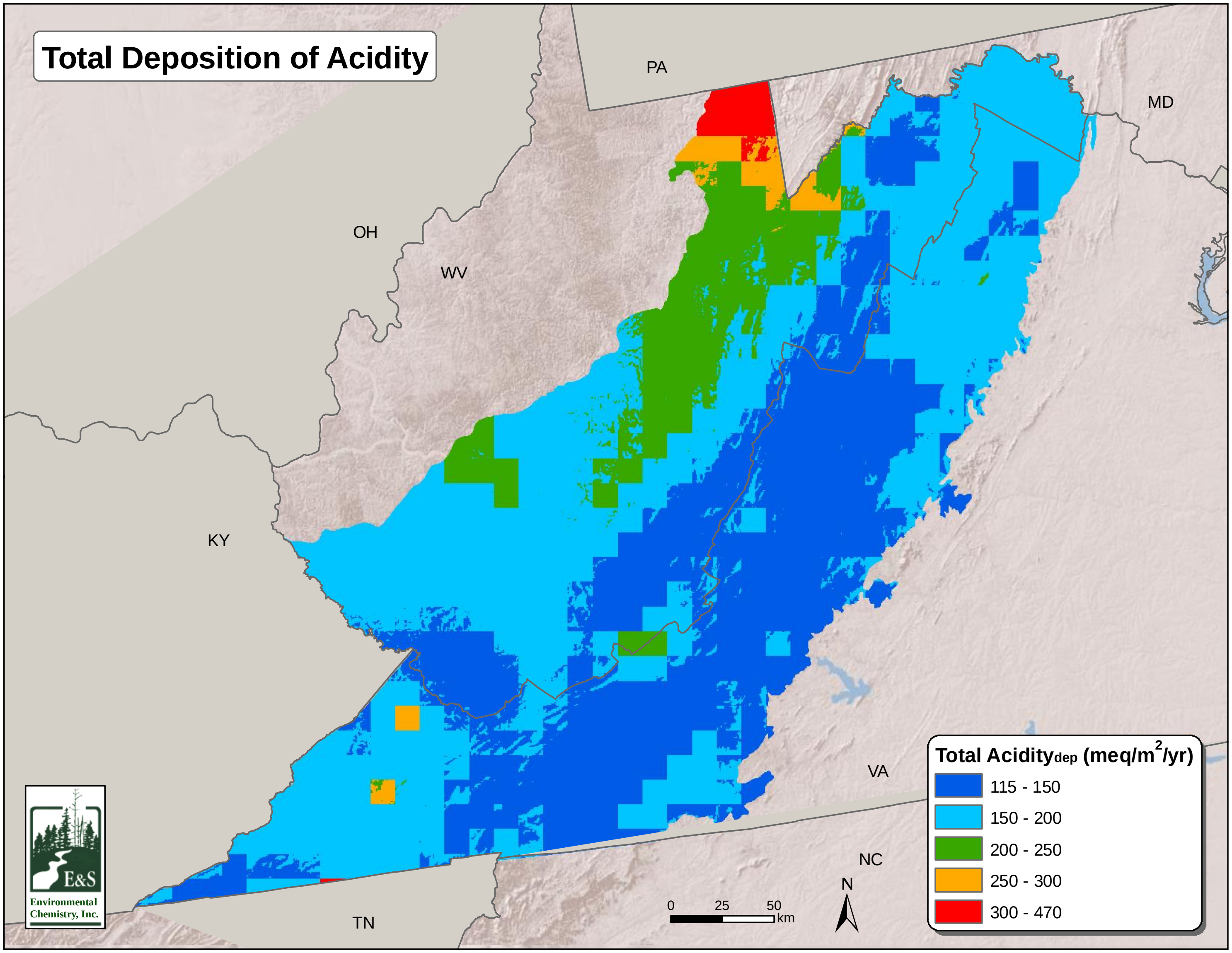


Figure 42. Total deposition of acidity across the study area, estimated from interpolated NADP wet deposition using the Grimm and Lynch (1997) approach (five-year average centered on 2002; E. Grimm, unpublished data) added to dry deposition estimates for 2002 from the CMAQ model (Robin Dennis, U.S. EPA, unpublished data).

4.4 Policy Considerations

Although process-based watershed models such as MAGIC and steady-state models such as SSWC entail uncertainty (cf., Sullivan et al. 2004, Li and McNulty 2007), results of CL calculations presented here will help to inform the development of the CL process as an important assessment and policy tool in the United States. This could aid the management of aquatic resources in acid-sensitive regions throughout the country. The approach may also be useful for addressing transboundary air pollution issues affecting Canada and Mexico. Additional logical steps in the process could include selection of interim (politically-determined) target loads of S deposition which would allow acid-impacted streams to begin the process of chemical recovery and move toward the long-term CL values that would sustain sensitive aquatic life forms. Critical loads models have been important tools for development of control strategies for transboundary air pollution in Europe (Gregor et al. 2001).

Science and policy are closely coupled in the CLs process. The scientific elements include tasks such as relating ambient air quality to pollutant deposition, quantifying the relationships between pollutant deposition and resource responses, identifying the resources at risk to adverse effects, understanding the temporal and spatial responses of resources to pollutant deposition, and more. The policy-dependent elements include tasks such as identifying the environmental resources to be protected, establishing appropriate criteria for different land use areas (e.g., Class I areas, national parks, wildlife refuges), and defining significant harm to protected resources.

There is, therefore, no single “definitive” CL for a natural resource. Critical load estimates are explicitly linked to policy, but their reliability is conditioned on the soundness of the underlying science. As elements of the CL process change, the CL estimates will change to reflect both the current state of knowledge and policy priorities. Changes in scientific understanding may include new dose-response relationships, better resource maps and inventories, larger survey datasets, continuing time series monitoring, improved numerical models, etc. Changes in the policy elements may include new definitions of harm, new mandates for resource protection, focus on new pollutants, or inclusion of perceived new threats that may exacerbate the pollutant effects (e.g., climate change). The CL process is thus an iterative process. As science changes, the scientific content is updated; as policy needs change, the content is re-directed.

The use of CL in resource management always has some time frame of expected response, and some context of management priorities. For instance, it may be that a deposition load well below the CL would hasten the recovery of a receptor that exhibits existing harm. Or, it may be that a receptor that has not yet been damaged can sustain a deposition load above the CL for some finite period before incurring significant harm. Such time frames can be very long (many decades or centuries).

The lack of explicit consideration of time in a steady state CL analysis can lead to assumptions that are not warranted. The CL derived in a steady state analysis is an estimate of the long-term, constant deposition that a receptor can tolerate with no significant harm after it has equilibrated with the CL deposition level. However, as shown by the analyses presented here, biological and geochemical processes that affect a receptor may delay the attainment of equilibrium (steady state condition) for centuries. By definition, steady state CLs do not provide any information on these time scales. Therefore, one cannot assume that reducing deposition to, or below, the steady state CL value will immediately, or within any management time period, eliminate or mitigate significant harm.

Calculated CL, combined with other temporal, economic, and/or political considerations, can be used to set short-term or long-term deposition targets. For example, a target load (TL) can be set on the basis of the CL, also considering issues of recovery response times. A TL can incorporate various management objectives. If the CL for resource recovery has been estimated to be x, one may set a TL equal to 1.5 x (or some other value) as an interim target with the intention of reaching the TL within a certain number of years. This interim target, although higher than the CL, might be considerably lower than ambient deposition, thereby allowing for partial resource recovery within a finite time period. The TL could also be set lower than the CL, for example if managers are unwilling to wait the decades or centuries that it might take to attain the threshold ANC value condition under constant loading at the CL level. The calculated CL values, such as are reported here for streams in Virginia and West Virginia, can provide the scientific foundation for policy judgments and the setting of TLs.

5.0 SUMMARY

Regional aquatic CL modeling was conducted using a modified version of the SSWC steady state model for streams in the Blue Ridge, Ridge and Valley, and Central Appalachian ecoregions in Virginia and West Virginia. A novel approach was employed to estimate the

weathering term, the key parameter in the SSWC model, based on calibration of weathering using a dynamic process-based model (MAGIC), with subsequent extrapolation of those weathering estimates to the entire study domain. Results indicated that substantial portions of the study area, and of the stream length within the study area, have relatively low CL values (less than 100 meq/m^2/yr). Ambient levels of atmospheric deposition acidity are in exceedance of the calculated CLs for half or more of the stream length within the region. In general, calculated CLs were lower, and exceedances were higher, in the Blue Ridge ecoregion, as compared with the Ridge and Valley and the Central Appalachian ecoregions. These steady state CL estimates are time invariant. Model projections using the dynamic MAGIC model suggested that most of the modeled watersheds will not reach steady state with respect to deposition acidity for hundreds of years. Therefore, reducing ambient deposition to the calculated CL levels may not result in recovery of water chemistry to levels protective of aquatic biota within the timeline of management decision making.

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